

OPTICAL STUDIES OF PRECIPITATION
IN DILUTE COPPER-COBALT ALLOYS
USING DIFFERENTIAL REFLECTOMETRY

By

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Differential reflectometry has been successfully applied to the study of precipitation in dilute copper-cobalt alloys. Experiments were designed to exploit the capability of the differential reflectometer to measure the difference in solute content between two alloys based on an altered electronic structure.

Composition modulation was performed in order to determine the effects that solid solutions of cobalt in copper have on the optical properties of the dilute alloys. It has been observed that the energy of the threshold electronic transition in copper at 2.2 eV has no dependence on the cobalt solid solution content. This lack of dependency has

been compared to similar results for nickel in copper, a phenomenon which has been treated by others with the theory of virtual-bound-states. It has also been determined that the strength of the differential reflectometric signal has a linear dependence at 2.2 eV on the difference in solid solution cobalt content between the two samples measured by this method.

Differential reflectometry was then applied to the study of aged copper-cobalt alloys. Three alloy compositions were used in these experiments: Cu-2.7 a/o Co, Cu-2.0 a/o Co, and Cu-1.0 a/o Co. The precipitation reaction was observed for all compositions at three aging temperatures: 600°C, 500°C, and 400°C. Additionally, Cu-2.7 a/o Co was aged at 550°C and 450°C. The precipitation reaction was followed by means of the increase in the strength of the optical signal which resulted from a decrease in the matrix solute content as the reaction progressed. A site saturated, diffusion controlled growth rate was observed for all compositions. The precipitates have been found to decrease the strength of the optical signal in a way which is linearly dependent on the volume fraction of the precipitates, thus allowing a measure of the microstructural state of an alloy to be obtained from measurements of the optical properties.

Microhardness measurements were performed on these aged alloys to provide an independent verification of the optical results. These microhardness measurements were in good temporal agreement with the optical measurements of this work

and with the results of previous measurements of mechanical properties of aged copper-cobalt alloys.

CHAPTER 1 INTRODUCTION

The color of alloys of metals has from ancient times been recognized as being influenced by the composition of the alloys. Artisans of many cultures surely experimented with combinations of metals in order to achieve the color they desired in the pieces they created. It was not until this century, however, that the link between the composition of an alloy and its color was understood.¹ With the development of solid state physics came the realization that the optical properties of metals and alloys are a reflection of their electronic structure, specifically the valence band.²

One instrument which has been successful in measuring the optical properties of alloys in order that electronic structure could be better understood is the differential reflectometer.^{3,4} With this instrument, the electronic structures of copper alloys containing multivalent solutes,^{5,6,7} copper-nickel,⁷ copper-gold,⁵ noble metal alloys,^{5,8} and nickel-based alloys^{9,10} have been investigated for composition dependence. In addition the effect on the electronic structure of the arrangement of constituents within alloys has been explored in studies of long range order¹¹ and short range order.¹² Finally, the removal of

an element from an alloy has been observed in experiments dealing with dezincification in brasses.¹³

Precipitation from a solid solution is a decomposition from a metastable one phase system to a two phase system. This reaction is characterized by the rejection of solute atoms by the matrix in order that a second phase be formed. This rearrangement of solute within the alloy would be expected to change the physical properties of the alloy. This is indeed the case. The measurement of electric,^{14,15} magnetic,^{16,17,18} thermal,¹⁹ and dimensional properties^{20,21} have often been used to follow the course of a precipitation reaction. The use of these methods exploits a particular sensitivity to some aspect of the physical changes occurring during a precipitation reaction. None of these methods can provide a complete description of the phenomenon. However, differential reflectometry has the capability, because of its extreme sensitivity to composition, of following a precipitation reaction from start to finish. This work will be devoted to the study by differential reflectometry of precipitation in dilute copper-cobalt alloys.

In the next chapter, a review of the literature is presented in three sections. The first section deals with the phenomenon of precipitation in a general way. In this manner, some understanding of this solid state reaction can be reached before the specific system of dilute copper-cobalt alloys is presented in the second section. A short analysis of the methods used for studying precipitation in

this system will also be presented here. The last section of this chapter focusses on the optical properties of copper and copper alloys. More specifically, the relationship between the composition of copper alloys and its electron band structure is explored.

Three types of experiments were performed in order to accomplish the goal of this work. Firstly, microhardness tests were performed on precipitation hardened alloys. Secondly, optical measurements were carried out on samples which were known to differ in composition only. Lastly, optical measurements were performed on samples which had experienced a precipitation reaction. The details of these experiments and the justification for performing them in this manner are given in the third chapter.

Presented in the fourth chapter are the results of these experiments as well as a discussion of the findings. Each set of results will be evaluated in terms of what other researchers have found in their studies of precipitation hardening in copper-cobalt as well as in terms of how the results compare against each other. In addition, a section on the effect of cobalt on the electronic structure of copper is presented.

The final chapter summarizes the findings of these experiments.

CHAPTER 2 OBSERVATIONS CONCERNING PRECIPITATION AND OPTICAL PROPERTIES OF ALLOYS

2.1 Precipitation: General

Since the end of the first decade of this century, when Alfred Wilm²² first demonstrated the means by which certain aluminum alloys could be strengthened, precipitation hardening has been used by metallurgists and materials scientists to improve the mechanical properties of the alloys of many base metals. Although aluminum-based alloys, particularly with additions of copper and magnesium, have probably been the most studied of all precipitation hardenable alloys, precipitation heat treatments are commonly used in many commercial alloys. Two notable examples are the addition of copper to malleable cast iron and the addition of titanium and aluminum to both semi-austenitic stainless steels and nickel-based superalloys.

Precipitation hardening is a process by which the mechanical and physical properties of an alloy can be dramatically altered. Performed under controlled conditions the strength and hardness of an alloy can be considerably increased. For instance, in a commonly used copper-beryllium alloy -- Cu-1.7 wt/o Be, 0.3 wt/o Co -- precipitation hardening can produce an increase in tensile strength from

410 MPa to 1030 MPa while at the same time increasing the hardness from 125 to 310 on the Vickers hardness scale. Changes in physical properties are also manifested by alloys during precipitation. In general, a significant increase in electrical and thermal conductivity along with changes in volume, magnetic properties, Hall coefficient and optical properties can be observed during precipitation. What follows is a simple description of phenomena which pertain to precipitation and the methods by which they are studied. Greater detail on particular subjects can be found elsewhere.²³⁻²⁷

The objective in producing a precipitation reaction is to induce the nucleation and growth of a second phase from a metastable solid solution. The reaction is expressed in the following manner, $\alpha \rightarrow \alpha + \beta$ where α is a solid solution and β is the precipitated phase. Although the formation of the second phase can be accomplished by changes in pressure or additions of another element, precipitation is most commonly carried out by the application of specific heat treatments, the details of which are given below.

The requirements to produce precipitation hardening (or age hardening) are that the alloying element is capable of achieving a solid solution, usually up to at least a few percent, with the base metal and that the solubility for the alloying element decreases with temperature. (In fact, there is another definitive requirement in order for precipitation hardening to be present, which is that the

alloy actually hardens as a result of the precipitation reaction.) In Figure 2-1, a phase diagram for a hypothetical age hardenable alloy has been drawn. It can be seen that the two requirements mentioned above have been met. To achieve precipitation, an alloy, which contains a few percent (C^0) of element B is held at T_s , the solution heat treatment temperature. This solution heat treatment allows all of element B to exist in a solid solution of the α phase. If the alloy is then quenched quickly enough to T_q , usually room temperature, the alloying element B can be made to remain in a metastable solid solution. In order to induce precipitation, the alloy is given an isothermal aging heat treatment at T_a . At this temperature, the metastable phase decomposes into two phases, α and β , approaching the composition defined by the phase diagram. During this decomposition, the matrix phase α rejects B atoms which go to form the β phase having a concentration C^β , which consequently lowers the matrix concentration of element B to the saturated state C^α . The amount of the second phase produced is determined by the tie line established by the aging temperature. At the completion of the reaction, the percent of β phase is

$$\% \beta = \frac{C^0 - C^\alpha}{C^\beta - C^\alpha} \times 100\%. \quad (1)$$

The precipitation reaction is generally considered to proceed in three stages: nucleation, growth, and coarsening. A brief, qualitative overview of these processes is given

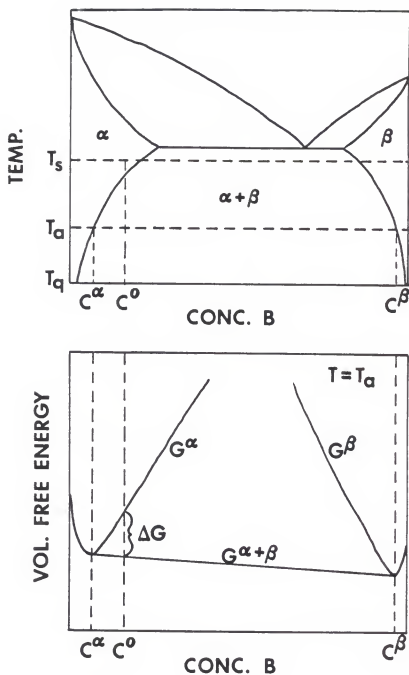


Figure 2-1. Phase Diagram of Hypothetical Precipitation Hardenable Alloy and Corresponding Free Energy Diagram.

here in order to provide a basis from which the specifics of the copper-cobalt precipitation reaction will be discussed.

When an alloy is held at a temperature at which its solute composition extends beyond the solvus, the lattice will reject solute atoms. As the solute atoms are rejected, they will begin to form clusters. This is the first stage of precipitation and is called nucleation. Thermodynamically, nucleation is driven by the difference in the volume free energy of the solid solution and the volume free energy of the decomposed system consisting of the precipitate phase and the matrix phase which is still a solid solution, though possessing a reduced solute content. Schematically, this is shown in Figure 2-1. The α phase at c° can be seen to possess a higher free energy, G^α , than the free energy of the decomposed system, $G^{\alpha+\beta}$. If, as is the case of precipitation hardenable alloys, the solubility decreases with temperature, then the difference in the free energies, ΔG , will increase the farther the alloy is held below the solvus (the greater the undercooling). This increases the nucleation rate and decreases the size to which a cluster must grow before it becomes stable and capable of increasing its size through growth. In general it is held that there are two "energies" which oppose the formation of stable clusters: surface energy and strain energy. When a cluster forms, it must eventually form an interface with the surrounding matrix. Because surface energy is added

to the system with the creation of this interface, the volume free energy difference, ΔG , driving the reaction must be large enough to compensate for this additional energy. Also, because the precipitates are composed of atoms of a different size than the matrix and have a different lattice parameter than the matrix, they create strain in the lattice. This strain energy must also be offset by the volume free energy reduction.

Nucleation is also influenced by the number of sites available for the formation of second phase particles. Because of the difference in size of the atoms of the precipitates and the matrix, formation of the second phase is favored at locations where strain can be readily accommodated, such as grain boundaries or dislocations. For this reason, nucleation will normally occur more rapidly in a fine grained or a heavily cold worked material where there are many sites at which precipitates can begin to form.

The same forces which operate in the nucleation of stable particles continue to operate during their growth. That is to say, the driving force continues to be a reduction in the volume free energy of the system with the product being a decomposed solid solution with precipitate particles interspersed throughout the alloy. The creation of new surface and the strain added to the system by growing particles also continue to influence precipitate growth. The balance between these forces will determine the shape of the precipitates, such that they try to achieve the

lowest energy configuration. For instance, in the early stages of growth small precipitates may form on planes which have low strain but a high surface energy. As the planes grow the surface energy becomes very large and the precipitates may change their shape to spheres which possess lower surface energy, but which also produce more strain in the lattice. The stages intermediate to achieving a final shape are called transition lattices.

In terms of composition, the growth of precipitates is accomplished by a depletion from the matrix of solute atoms from the concentration C^0 , the supersaturated concentration, to C^α , the concentration of solute atoms at the solubility limit. The classic, phenomenological approach to this process finds that the time dependence of the matrix composition is expressed as

$$\bar{C}(t) = C^\alpha + (C^0 - C^\alpha)e^{(-t/\tau)^n} \quad (2)$$

where $C(t)$ is the solute concentration at time t , τ is a time constant, and n is dependent upon the particulars of the growth process.

Although the kinetics of the precipitation reaction can be very complicated, there are some rules that apply in general to the reaction rate. Growth of the precipitate is often controlled by the diffusion of solute atoms through the matrix to the precipitate. For this reason, the precipitation rate is faster at higher aging heat treatment temperatures. In addition, because diffusion is controlled

by the number of vacancies, dislocations, and other lattice defects, growth will normally occur more rapidly in an alloy which has experienced a rapid quench, heavy cold work, or radiation damage than in an alloy in which these conditions are not present.

Coarsening refers to the increase in interparticle spacing which has been found to occur during the final steps of precipitation reactions. It is most easily described by the familiar axiom of materials science, "Large particles grow at the expense of smaller ones." In contrast to nucleation and growth, which were driven by the lowering of the volume free energy in going from a supersaturated solution to a decomposed two phase system, coarsening is driven by a reduction in surface energy. It is generally considered to occur after all chemically-driven growth has stopped, with no change in the volume fraction of second phase. Given these considerations, it can be seen that coarsening is also characterized by a decrease in the number of precipitates and an increase in the average particle size with time.

Precipitation is also characterized by the distribution of the second phase throughout the matrix. In what is known as general precipitation, the precipitate is distributed randomly throughout the matrix. The reaction occurs simultaneously in all parts of the matrix. The result of this is a uniform precipitate structure.

In contrast to this, localized precipitation is characterized by growth of precipitates at lattice defects or

grain boundaries. Similar to general precipitation, it occurs simultaneously throughout the alloy; however, because the precipitates form at defects, the precipitates are distributed non-uniformly.

Finally, discontinuous precipitation is characterized²⁵ by the formation of second phase in random parts of the alloy at random times. Discontinuous precipitation is associated with the movement of an interface, such as a grain boundary during recrystallization and grain growth.

The effect of precipitation on mechanical properties depends on several microstructural aspects, such as the extent of the solid solution, the coherency of the precipitate, the dispersion of the second phase, and recrystallization.²⁴ All mechanical properties are affected by these microstructural factors; however, for the reason that microhardness tests were performed for this work, the changes in hardness experienced by an alloy undergoing a precipitation reaction will now be considered. In Figure 2-2, a composite hardness curve is depicted with the contributions from each microstructural factor also shown. The details of this graph are discussed below.

Solid solution hardening takes place because the difference in size between the atoms of the host metal and the solute atoms necessitates the accommodation of solute atoms at places where strain is introduced the least. As mentioned earlier, this means that solute atoms collect at defects in the lattice such as dislocations and grain boundaries.

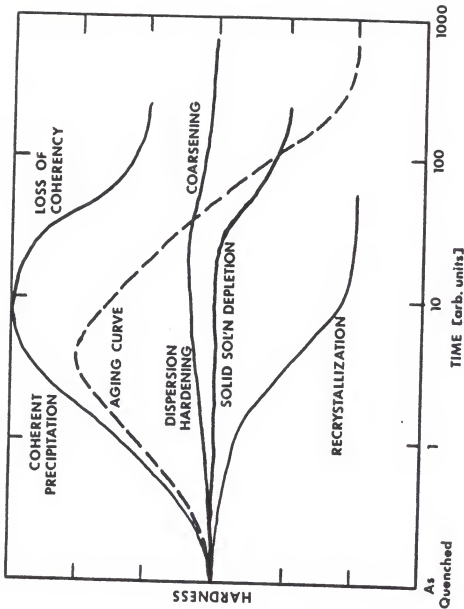


Figure 2-2. Composite Hardness Curve. (Ref. 24)

By collecting at dislocations, solute atoms pin them and prevent them from moving during an applied stress. In addition, solute atoms can either replace solvent atoms on regular lattice sites (substitution) or they can occupy sites between lattice positions (interstitial). In either case, the solute atom will create strain in the lattice, which impedes the movement of dislocations. These mechanisms account for the increase in hardness upon the addition of solute atoms to an alloy. During a precipitation reaction, solute atoms are removed from the matrix in order to form the precipitates. Thus as shown in Figure 2-2, as the aging of the alloy progresses solid solution hardening decreases.

The most important contribution to the hardening of an alloy during precipitation comes from coherent precipitates. In the case of general precipitation the first precipitates to form are coherent with the lattice, that is, the lattice of the precipitate matches point for point the lattice of the matrix. Such clusters of a relatively large number of atoms of different size than the matrix exert strain which extends well beyond the immediate vicinity of the precipitates. As long as coherency is maintained, the larger the precipitate becomes, the more strain is exerted on the lattice. The interaction of a moving dislocation with this strain field requires more energy for movement than if there were no precipitate. Thus a dramatic increase in hardness is seen in Figure 2-2 upon the formation of coherent precipitates. As the decomposition proceeds, the

precipitates become so large as to require dislocations to maintain a limited amount of coherency with the lattice. This is called a "quasi-coherent" state²⁷ and marks the beginning of the formation of an interface. As the precipitation continues, the particles become large enough to require a definite interface between the growing precipitate and the matrix. At this stage, the precipitate is completely incoherent with the matrix, and dislocations at the interface between the particle and the matrix accommodate the strain produced by the precipitate. Thus, the effect of the precipitate on the movement of dislocations is diminished, and there is consequently a dramatic loss in hardness.

Dispersion hardening arises from the fact that at the beginning of the process there are many particles spaced fairly close together. As precipitation continues, coarsening can occur with larger particles growing at the expense of smaller ones, causing the precipitate structure to evolve to one in which there are fewer particles spaced farther apart. This process accounts for the slight rise in hardness followed by the slight softening seen in Figure 2-2.

The final factor that affects the composite hardness curve is recrystallization of the alloy. This is a complicated phenomenon, which itself is influenced by many factors. These include aging temperature, aging time, amount of deformation, composition, and grain size. It is necessary,

but hardly sufficient, to state that if recrystallization occurs during aging, the result will always be a loss of hardness brought about by the replacement of deformed, and therefore hard, grains by undeformed, softer grains.

Changes in the physical properties of alloys undergoing precipitation have long been observed and used as tools to measure the kinetics of the reaction and to help to determine the mechanisms by which the reaction takes place. Although these measurements are indirect, at the very least, the measurement of physical properties yields the initial state of the alloy, the changes that occur during the reaction, and the point at which the reaction is complete.

Measurements of resistivity, saturation magnetization, Curie temperature and density or volume are common techniques in studying precipitation. These methods fall into two categories. Firstly, there are those which follow the growth of the second phase, as in the case of a magnetic second phase precipitating from a non-magnetic matrix. Here, measurements of magnetic saturation or coercive force are used in determining the details of the reaction. Secondly, there are studies which follow the depletion of solute from the matrix phase. This type of experiment might be used in the case of a magnetic matrix phase and a non-magnetic second phase, where the rise in the Curie temperature could be measured to determine the rate at which solute was being removed from the matrix by precipitation.

Another example, where the removal of solute is measured, is electrical resistivity measurements. Figure 2-3 shows a resistivity curve for a hypothetical alloy. As is shown, the resistivity of the precipitation hardenable alloy is dependent on two variables, the depletion of the solid solution and the coherency strains produced by the precipitate. Here, unlike the case of hardness where the extent of coherency was the dominant factor, the solid solution depletion is more important. As solute atoms are rejected by the matrix in order to form second phase particles, the number of electronic scattering centers is reduced, thus lowering the resistivity. The extended strain field of coherent particles acts to increase the resistivity of the alloy. However, as the precipitates grow and become incoherent, the lattice returns to a more relaxed state and the resistivity consequently decreases.

2.2 Precipitation in Dilute Copper-Cobalt Alloys

Interest in the copper-cobalt system as an example of a precipitation hardenable alloy, although never as intense as in the more commercially important aluminum age hardenable alloys, has nonetheless been steady.^{16,28-48} One of the reasons for this lies in the simplicity of the copper-cobalt system, the phase diagram of which can be seen in Figure 2-4.⁴⁹ The copper-cobalt phase diagram shows a miscibility gap with a peritectic transformation on the

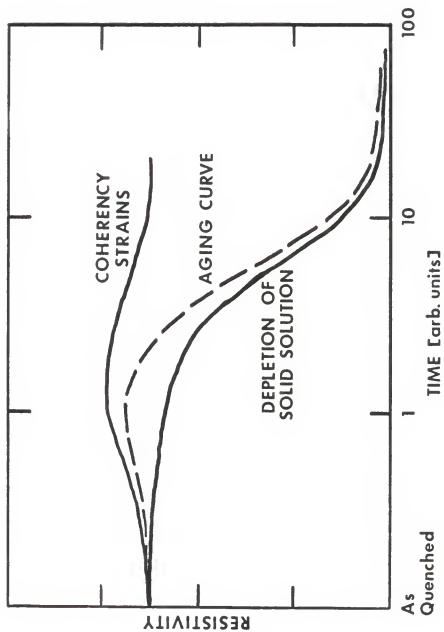


Figure 2-3. Composite Curve showing the Effect of Precipitation on Electrical Resistivity. (Ref. 24)

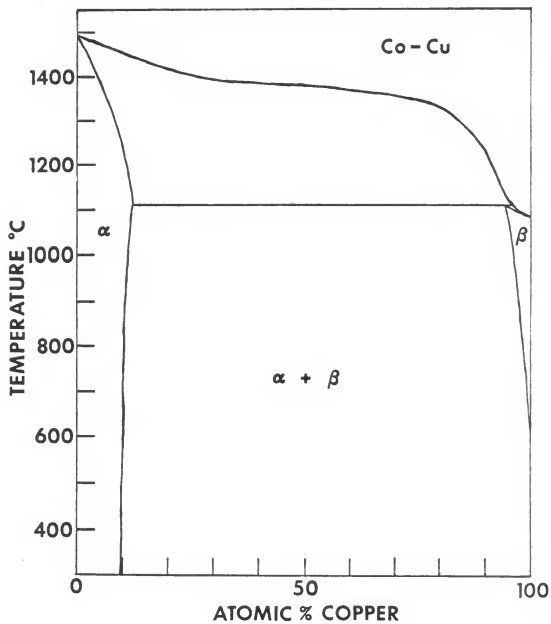


Figure 2-4. Phase Diagram of Copper-Cobalt System.
(Ref. 49)

copper-rich side. The peritectic temperature is 1110°C , at which is also found the maximum solubility for cobalt in copper. It is this region of solid solubility on the copper-rich side of the phase diagram to which attention is focused when precipitation hardening is being considered. It is evident that this region possesses the primary condition necessary to achieve age hardening, that is, a decreasing solubility for cobalt with decreasing temperature. Solubility drops from about 5.5 wt/o at 1110°C to below 0.1 wt/o at 500°C . Experiments conducted on dilute copper-cobalt alloys have generally employed alloy compositions ranging from slightly below 1.0 wt/o to about 3.0 wt/o. The range of aging temperatures investigated extends from 400°C to 700°C , concentrating attention around 600°C . The fact that these alloys age at such moderately high temperatures is advantageous for the experimenter because the alloys will not age at room temperature.³⁷

The precipitate that forms in these alloys upon aging can be seen by the phase diagram to be a cobalt solid solution containing approximately 10 wt/o copper. This precipitate, containing such a large amount of cobalt, is ferromagnetic.^{16,27-29,50-51} The precipitate has been found to possess an FCC structure and to form as a spherical particle.^{17,51-52} No intermediate lattices or shapes have been noted.³⁴ The dominant precipitation mode is a general precipitation, although some localized and discontinuous precipitation have been observed.^{27,33,47} Only in the

extremely overaged condition has a shape change in the precipitate been observed,¹⁷ that being from spheres to plates.

As stated above, the cobalt-rich precipitate which forms during aging contains enough cobalt for the precipitate to possess ferromagnetism. Prior to coalescence, cobalt atoms do not have a ferromagnetic character due to the absence of a sufficient exchange interaction with neighboring cobalt atoms.^{53,54} Thus as precipitation occurs the magnetic state of the alloy changes from diamagnetic to ferromagnetic. Becker¹⁶ used the term "superparamagnetic" for the latter condition. As the precipitates grow, the magnetic coupling of the cobalt atoms becomes stronger and the saturation magnetization of the alloy becomes larger. From this, Becker¹⁶ and others^{29-31,33,36,41,44} were able to deduce the volume of precipitate formed, the radius of the average precipitate, and the volume fraction of precipitate.

From magnetic measurements on a Cu-2% Co alloy aged at 600°C, Livingston and Becker²⁹ concluded that all of the cobalt was precipitated during the first few minutes of aging and that subsequent growth of the precipitates took place by coarsening, a process in which the total volume and the volume fraction of precipitate remained constant after the first few minutes of aging. They also concluded that the radius of the precipitate increased linearly with the logarithm of aging time. This same conclusion was reached by Witt and Gerold³⁷ for copper alloys containing

1.4%, 2.0%, and 3.0% cobalt when aged at 600°C. However, in the same experiment, analysis of their data reveals that for Cu-0.6% Co the volume fraction increased linearly with time up to 32 hours of aging at 600°C.

It was also through the use of magnetic measurements that experimenters concluded that the precipitates were spherical.^{17,52} This conclusion was reached on the basis of only very slight magnetic anisotropy observed in the aged single crystal alloys. Finally, the lattice of the cobalt-rich precipitate has been found to be 2% smaller than the lattice of the matrix.⁵⁵

In another study of precipitation in copper-cobalt, Servi and Turnbull³⁸ aged the various alloys at temperatures such that the solute composition did not deviate much from equilibrium. This was performed in order to determine the effect of undercooling upon the nucleation rate. By following the change in resistivity, they obtained a measure of the volume fraction transformed through the use of Equation 3 and the relation

$$X = \frac{C^0 - \bar{C}(t)}{C^0 - C^{\alpha}} \quad (3)$$

where X is the volume fraction transformed. Although the transformation was observed to begin very shortly after aging was started, analysis of the data indicates that full transformation was never achieved, in contrast to what was observed in the magnetic studies cited above. The data did, however, confirm the growth of spherical precipitates.

A more direct method of observing precipitation in copper-cobalt alloys has been carried out by a number of researchers.³¹⁻³⁵ This is the observation of coherency strains in the lattice caused by the precipitates and detected by means of transmission electron microscopy (TEM). The TEM theory of diffraction contrast was used to obtain particle diameters from the "double D" diffracted image, which is the signature of spherical, coherent particles. Here, as in the case of magnetic measurements, the radii of growing particles increased linearly with the logarithm of aging time.³³ Observations that the number of precipitates seen in the micrographs decreased with time were attributed to coarsening,^{33,34} although the data were never quantitatively compared to coarsening theory. Likewise, no quantitative comparison was made between this work and previous magnetic measurements, which had also indicated growth by coarsening.

TEM observations have indicated in quenched alloys that a complete solid solution with no formation of precipitates is possible to achieve. Phillips and Livingston³¹ have shown that no precipitates were observable in solution heat treated and quenched alloys. They also noted that precipitates were seen shortly after the aging heat treatment was begun.

As was discussed in Section 2.1, mechanical properties, such as hardness, yield strength, and tensile strength, tend to rise from the onset of precipitation, go through a peak,

which is influenced to the greatest extent by coherency of the precipitate, and then decline as the alloy softens when the precipitates grow too large to maintain their coherency. Softening is also the result of the coarsening of the precipitate structure when the interparticle spacing becomes too large to prevent easy motion by dislocations.

Copper-cobalt is not an exception to these mechanisms. In Figures 2-5 and 2-6, data from Livingston and Becker²⁹ and Livingston³⁰ are presented. In these curves are displayed characteristics which are typical of a precipitation reaction. In Figure 2-5,²⁹ data for a Cu-2% Co alloy aged at 600°C are presented. An increase in hardness is observed as the alloy is aged up to approximately fifteen hours, at which point a peak hardness is obtained. Past this peak, the loss of coherency of the precipitate with the lattice causes softening to occur. In Figure 2-6,³⁰ yield strength and hardness data for a Cu-2% Co alloy aged at 600°C, 650°C and 700°C are presented. Here, several observations can be made which reveal the characteristics of the precipitation process in copper-cobalt. Not only are peaks seen to occur at each aging temperature in both yield strength and hardness, but it is also evident that as the aging temperature is increased, the time for each mechanical property to reach its peak is reduced. This is a consequence of the increased diffusion rate as temperature is increased. The faster diffusion occurs, the faster the precipitates can form. Finally, as the aging temperature is reduced, the higher

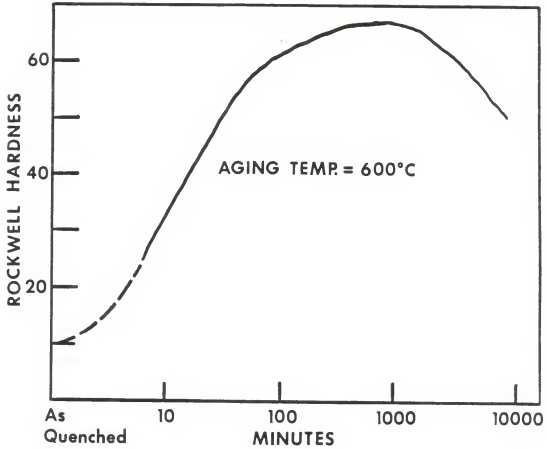


Figure 2-5. Hardness versus Time for Cu-2.0% Co Alloy Aged at 600°C. (Ref. 29)

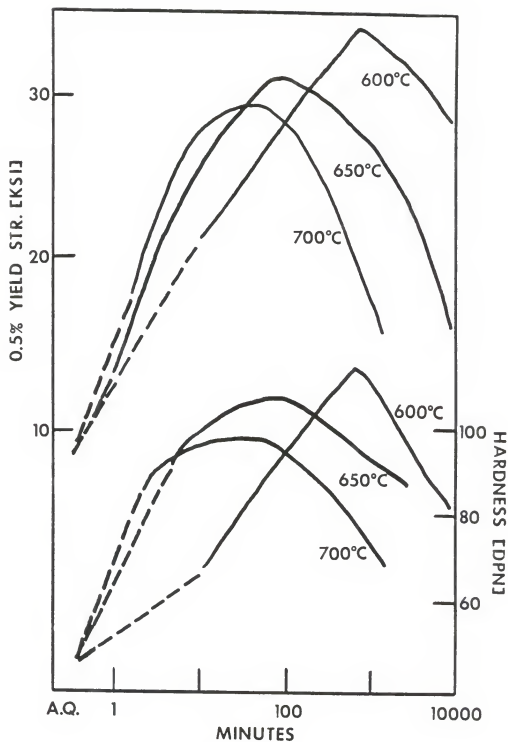


Figure 2-6. Yield Strength and Hardness versus Time for Cu-2.0% Co Aged at Various Temperatures. (Ref. 30)

the peak value of the yield stress and the hardness becomes. This was reported by Livingston³⁰ to be due to the reduced solubility at the lower temperature, which leads to a greater volume fraction of precipitate.

In Table 2-1 data are compiled from studies of the mechanical properties of copper-cobalt alloys. The table shows the aging temperature and length of time required to reach a peak in the particular property investigated. Most studies indicated that the higher the temperature at which the alloys were aged, the faster the growth of the precipitate. Perovic and Purdy,⁴⁷ in their investigation of precipitation in these alloys aged from 400°C to 800°C, found that the precipitate had a growth rate maximum between 550°C and 600°C.

There is some controversy concerning the length of time necessary to bring the precipitation reaction in this system to completion. This may be due to the fact that each of the methods used have sensitivities that are particular to certain aspects of the reaction. For example, whereas TEM does allow a direct observation of precipitate formation, compositional changes can not be determined quantitatively. No statistical methods have been applied which reveal whether the growth of precipitates is due to depletion of matrix solute or due to coarsening of the precipitate structure.

Because the precipitate in this system is ferromagnetic, magnetic measurements provide a method of following the growth of the precipitate. The model of Becker¹⁶ has generally been used to quantitatively determine the average radius

Table 2-1. Time to Peak Property
for Copper-Cobalt Precipitation

<u>Aging Temp.</u>	<u>% Co</u>	<u>Measurement</u>	<u>Time to Peak (hr)</u>	<u>Ref.</u>
250°C	3.2%	Hardness	> 1000	28
375°C	3.2%	Hardness	> 1000	28
550°C	2.0%	Yield Strength	160	30
	3.2%	Hardness	175	28
600°C	2.0%	Yield Strength	16	30
	2.0%	--	12	45
	2.0%	--	11	46
	3.1%	TEM (Coherency strains)	12	33
650°C	2.0%	Yield Strength	1.5	30
	2.0%	CRSS	4.0	44
	3.1%	TEM (Coherency strains)	1.5	33
	3.1%	Yield Strength	1.5	34
700°C	2.0%	Yield Strength	0.5	30
	2.0%	CRSS	1.0	44
	3.1%	TEM (Coherency strains)	0.7	33
	3.2%	Hardness	3.0	28

of the precipitate and the volume fraction transformed. However, this model assumes that no precipitate is larger than 10 nm and that there is an equal number of particles of each size in the distribution. The validity of these assumptions has not been independently established. Furthermore, the saturation magnetization continues to increase as the precipitates coarsen,¹⁶ and therefore, it is difficult to determine with precision when equilibrium has been reached.

Measurements of the electrical resistivity of alloys are useful for following the depletion of solute from the matrix, and have been used³⁸ in following the nucleation and growth of the second phase in this system. In following the depletion of solute from the matrix, however, this method offers little information about the precipitate and its effects on the physical properties of the alloy.

Measurements of the mechanical properties during precipitation are valuable in determining the microstructural state of the alloy, particularly whether or not the precipitate is coherent with the matrix. However, these methods provide only qualitative information about the extent of the transformation or the fraction transformed.

In contrast, differential reflectometry offers a method that can be sensitive to both the changing solute concentration of the matrix and the formation of the second phase. This sensitivity is not limited fundamentally as is the case in the other experimental techniques.

To conclude, the investigations of precipitation in the

copper-cobalt system have revealed a fairly typical reaction. Although there is some discrepancy in the length of time measured for the reaction to achieve a fully transformed state -- that is, the point at which microstructural changes are due only to coarsening -- it has been observed that the precipitate produced is a sphere and has no intermediate shapes. Furthermore, the precipitates form throughout the matrix with some localized precipitation at the grain boundaries. The changes in mechanical properties during aging likewise have been seen to be representative of an age hardenable alloy. The ascent-peak-descent curves seen in the graphs of hardness vs. aging time for these alloys are the unmistakable fingerprint of precipitation. The generally good agreement between the data of these various research efforts reveals a well characterized system. These data also provide a backdrop against which the hardness tests described in this work can be compared.

2.3 Optical Properties of Copper and Copper Alloys

The effects of solute additions on the mechanical properties of metals have already been discussed. Some change in the yield strength, tensile strength, ductility, hardness, and impact strength is the inevitable consequence of altering the composition of a metal. Some changes may be beneficial as in the case of adding zinc to copper, thus producing an alloy that is both stronger and more ductile than pure

copper;⁵⁶ or the effect of alloying may be detrimental such as the brittleness that is produced when a small addition of iron is made to copper.⁵⁷

Physical properties are also very much a function of composition. Upon addition of another element to a pure metal, its melting point, density, electrical and thermal conductivity, magnetic and optical properties are affected. These property changes upon alloying are the direct result of an altered electronic band structure. This is particularly true of optical properties. In this section, the relationship of the optical properties of copper to its band structure will be considered. In addition, attention will be directed to the response of the band structure, and hence optical properties to composition changes and to methods by which these changes have been measured.

In Figure 2-7, the band diagram of pure copper is presented.⁵⁸ Because the electronic configuration of copper is $3d^{10}4s^1$, it is expected that the d-bands of copper would lie entirely below the Fermi energy. This is indeed the case, with the top of the d-bands lying slightly more than 2 eV below the Fermi energy. The partially filled s-bands and p-bands are labelled in the figure. When photons of sufficient energy are incident upon a metal, electrons from filled states are raised into unoccupied states above the Fermi energy. The result of these direct interband transitions can be seen in Figure 2-8,¹ where curve A depicts the optical reflectivity for pure copper as a function of

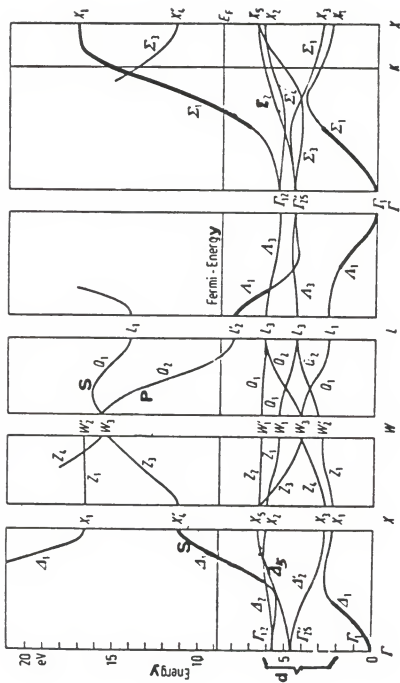


Figure 2-7. The Band Diagram of Copper (Ref. 58).

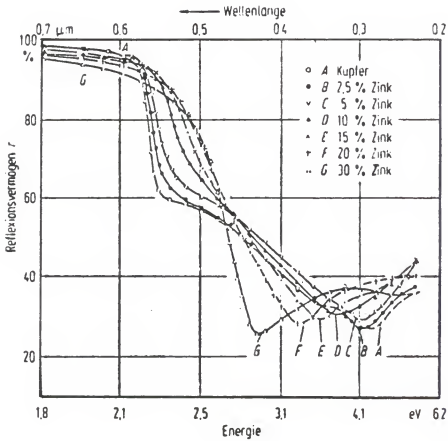


Figure 2-8. Reflectance Spectra for Copper and Various Brasses (Ref. 1).

energy. It is evident that at energies below 2.2 eV the reflectivity is close to 100%. However, at 2.2 eV light is absorbed initiating the first interband transition. These transitions, which occur from the upper d-bands to s-bands and p-bands at the Fermi energy, are believed to occur near the L symmetry point.⁵ These transitions also give rise to the characteristic salmon pink color of pure copper, since they produce a much lower reflectivity in the green and blue regions of the spectrum than in the yellow and red regions. Other transitions which influence the reflectivity of copper occur between the Fermi energy and the s-states (L_{21} to L_1) around 4.2 eV and between the lower d-bands and the Fermi energy at approximately 5.5 eV.⁵⁹

The influence of solute additions upon the reflectivity of copper can also be seen in Figure 2-8, which presents reflectivity spectra for various brasses. There is a drop in reflectivity in the energy range of 1.8 - 2.2 eV, as a result of the dependence of reflectivity upon resistivity expressed by the Hagen-Rubens relation:¹

$$R = 1 - 2(\nu\rho_0)^{\frac{1}{2}} \quad (4)$$

where R is the reflectivity, ν is the frequency of the incident radiation and ρ_0 is the dc resistivity. Since the addition of solute atoms increases the metal's resistivity by increasing the number of scattering centers, the reflectivity is consequently reduced. Although this empirical relation was discovered before there was any knowledge of band

diagrams and interband transitions, it still holds for those regions where no interband transitions occur.

In addition to this decreased reflectivity, the transition which occurs at 2.2 eV is shifted to higher energies as the zinc concentration in the brass is increased. This increase in the threshold energy causes the change in color in brasses from red at low zinc concentrations to yellow at high zinc concentrations. It has been found that upon alloying with elements having a valence of greater than one, that the subsequent energy increase of the threshold transition above 2.2 eV is caused by a rise in the Fermi energy due to the addition of extra electrons from these elements and to a narrowing and raising of the d-bands.^{5,60} The earliest attempt to explain the transition energy increase upon adding elements of higher valence than the host metal was proposed by Mott^{61,62} in 1935 in the rigid band model. Although the model did correctly predict the rise in the Fermi energy, it did not predict the shift that occurs in the d-band upon alloying. This led to a prediction of a larger shift in the transition energy at 2.2 eV than was seen experimentally. Calculations made by Bansil et al.⁶⁰ accounted for the shift upward in the d-bands as well as the Fermi energy and therefore the smaller shift in the threshold energy.

Hummel's laboratory^{5,6,7} has experimentally verified that the shift in the transition energy at 2.2 eV is smaller than that predicted by the rigid band model. Using a differential reflectometer, the energies of electronic

transitions were measured for copper solid solutions containing various multivalent alloy additions. It was found that the transition energy was a function of composition (see Figure 2-9).⁵ Up to 1% solute there is no change in the threshold energy. Past 1% solute, the transition energy is a linear function of composition. It is evident that Figure 2-9 can also be used as a calibration curve, so that if the transition energy of an unknown alloy is measured, then the quantity of solute in that alloy can be determined. Thus, it is possible to use optical measurements as a means of determining the solute concentration of a binary copper alloy. In the case of multivalent solutes in copper, of course, this method would only be useful for solute concentrations above one percent.

So far, the discussion has been directed only at alloys of copper which contained solutes having two or more valence electrons, where the increase in the Fermi energy could be understood on an intuitive basis. The situation becomes more complex when transition elements are added to copper. As an example of a copper-transition metal alloy, copper-nickel has been studied in great detail,^{7,63-66} because they display complete solid solubility. Since nickel has an unfilled d-band -- its electronic configuration is $3d^8 4s^2$ -- the intuitive expectation is that when nickel is added to copper, the copper 4s electron might supply the extra electrons necessary to fill the d-band of nickel. It would then be expected that the Fermi energy of copper would be lowered,

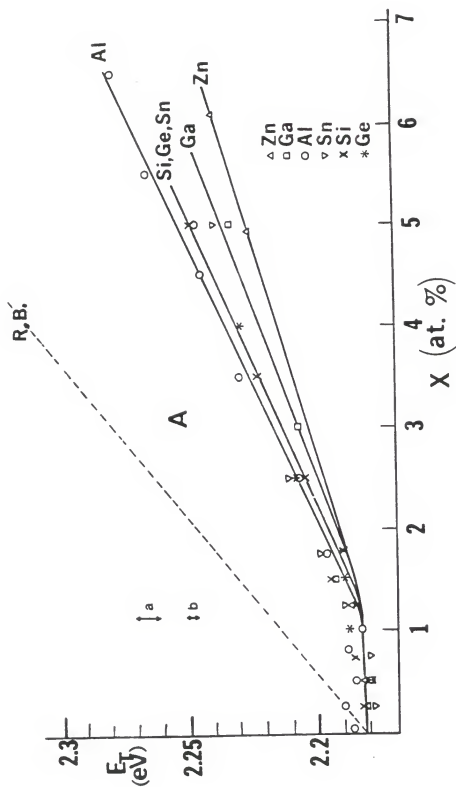


Figure 2-9. Composition Dependence of Copper Threshold Transition. (Ref. 5)

and accordingly the threshold energy for direct interband transitions would be decreased. These are the predictions of the rigid band model.⁶² Experimentally, however, it has been determined by means of optical measurements^{7,63} and photoelectron spectroscopy⁶³ that the transition energy at 2.2 eV in copper is unchanged by solute additions of nickel. Instead, evidence indicates that the nickel d-bands remain independent of the copper d-bands and that they retain their character within the matrix. These nickel d-bands are found to exist within one electron volt of the copper Fermi energy and become the source of low energy transitions. In Figure 2-10, the reflectance spectra from Seib and Spicer⁶³ for pure copper, Cu-13% Ni, and Cu-23% Ni are presented. In contrast to the reflectance spectra for copper-zinc alloys, there is no change in the transition energy at 2.2 eV as nickel is added to copper. There is a drop in reflectivity below 2.2 eV which is caused by transitions from the nickel d-bands to the Fermi energy, thus decreasing the magnitude of the 2.2 eV transition. These results verified the proposals of Friedel⁶⁷ and Anderson⁶⁸ who had predicted this type of behavior -- known as virtual-bound-states -- for transition elements in copper. It is clear that there is no composition dependence of the 2.2 eV transition, such as was the case in copper with multivalent solutes. Using photoemission Seib and Spicer⁶³ did find that the band width of the virtual-bound-states of nickel did increase as the amount of nickel increased.

Using differential reflectometry, Hummel et al.⁷ also

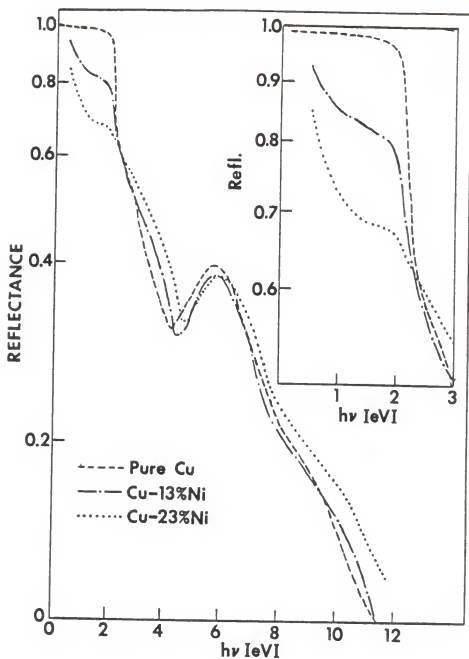


Figure 2-10. Reflectance Spectra for Copper and Two Copper-Nickel Alloys. (Ref. 63)

found no shift in energy of the threshold transition at 2.2 eV in copper-nickel alloys. The alloys studied in this work ranged from copper containing less than one percent nickel to greater than twelve percent nickel. This result, which confirmed the existence of virtual-bound-states in copper-nickel alloys, provided no strict method of determining the solute concentration of an unknown alloy. It was noted that the "sharpness" of the peak in the differential reflectogram associated with the 2.2 eV transition did possess a composition dependence. However, no definitive composition dependence was observed at 2.2 eV as in the case of copper containing multivalent solutes.^{5,6,7}

Beaglehole and Kunz⁶⁹ did find a composition dependence on the difference in reflectivity of various dilute copper-nickel alloys. Their data showed a linear relationship between the difference in reflectivity at 628 nm and the difference in the composition of the alloys measured, which agreed with that of other investigators.^{66,70,71} This linear relationship was found to be valid up to approximately 20% solute, demonstrating that optical measurement might be used to determine the composition of an alloy containing a transition element.

For the reason that this work centers on optical investigations of precipitation in copper-cobalt alloys and that the precipitates in this system are a cobalt solid solution -- approximately 90Co-10Cu -- it is necessary to consider the optical properties and the electronic structure of cobalt.

Cobalt is a transition metal and resides next to nickel in the periodic table. Its electronic configuration is $3d^7 4s^2$. Again, as in the case of nickel which has an unfilled d-band, the electronic band structure of cobalt is found to possess d-bands which contain both filled and unfilled states and which lie within a few electron volts of the Fermi energy.⁷²

-76 A high density of states, therefore, exists just above and just below the Fermi energy. Although quantum mechanical considerations can not be put aside, for all practical purposes, this large density of states around the Fermi energy can be considered to be a continuum. This implies firstly that electronic transitions can be stimulated by incident light at low energies, and secondly that an incremental increase in the energy of the incident light will be matched by an increase in the number of transitions stimulated. This can be seen in the reflectivity curve for cobalt (Figure 2-11), which was calculated from optical constants determined by Johnson and Christy.⁷⁷ The reflectivity is already below 80% at 1 eV, due to low energy optical absorption which stimulates d-band transitions. Also seen is a monotonic decrease in reflectivity caused by the stimulation of a greater number of transitions as the energy of the incident light is increased. In addition there is no sharp change in the reflectivity in the range of 1 eV to 6 eV indicative of interband transitions or plasma resonances.

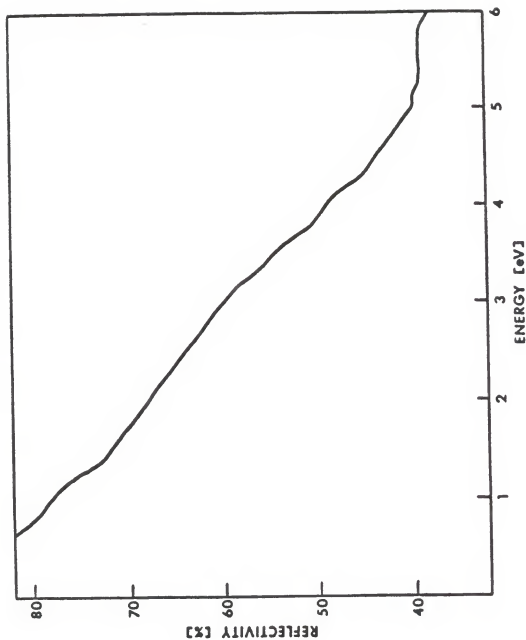


Figure 2-11. Reflectivity Spectrum for Cobalt as Calculated from Measurements of n and k by Johnson and Christy (Ref. 77).

CHAPTER 3 EXPERIMENTAL PROCEDURE

3.1 Experimental Approach

The experiments comprising this work on Cu-Co alloys fall into three categories. Firstly, differential reflectometry was performed on samples to establish spectra solely on composition differences, hereafter known as compositional modulation. Secondly, differential reflectometry was performed on samples which had been given various aging heat treatments. Finally, microhardness testing was performed upon samples to study the change in that mechanical property upon precipitation.

The purpose of performing the compositional modulation experiments was twofold. First, it was necessary to obtain spectra which were produced due specifically to composition differences between two samples. In the aging experiments carried out on the differential reflectometer, spectra were to be produced by the difference between an aged and a solution heat treated sample. For reasons that have already been described, the aged sample would have less cobalt in the alloy matrix. Thus at least some of this spectrum would be due to composition differences between the

aged and the unaged samples. By having composition modulation spectra, it becomes possible to identify which part(s) of the differential reflectometry spectra in the aging experiments were due to composition differences and which part(s) were due to some other aspect of aging which would produce a change in the optical properties of the alloys.

Second, by performing compositional modulation experiments, it is possible to obtain information about the effects of additions of Co upon the electronic structure of Cu. Although somewhat limited by the small solubility of Cu for Co, the predictions of the virtual-bound-state theory vs. the rigid band model could be investigated.

As was discussed in the last chapter, the changes in hardness that occur in an alloy during a precipitation reaction are well documented and well understood. As has already been discussed, hardness tests provide a clear, if indirect, method by which the kinetics of the precipitation reaction and the microstructural changes involved in that reaction can be interpreted. For this reason, microhardness tests were chosen as a method against which the results of the optical data could be compared and contrasted.

3.2 Alloy Preparation

All alloys used in these experiments were produced by combining appropriate amounts of Cu-2.7 at/o Co powder and pure Cu powder. The powders were blended and placed into

a graphite crucible for melting. A sodium borate flux was used to protect the melt from oxygen contamination. Because of the very narrow alpha plus liquid phase field (See Figure 2-4) segregation upon solidification was deemed not to be a problem and the ingots were allowed to solidify in the furnace. Upon removal from the crucible, each ingot was cleaned of any remaining flux and dipped for a few seconds into an etchant (5:1 nitric acid:water) to remove any surface contaminants. Each ingot was then rolled by 50%, recrystallized under vacuum at 350°C for one hour, and rolled again by approximately 33%. Each ingot was then placed in a graphite crucible and covered with sodium borate flux and given a solution heat treatment at 1000°C for approximately 70 hours. The ingots were then quenched in iced brine to complete the solution heat treatment. The ingots were then cleaned by etching and cut on a diamond wheel to a size of approximately 0.25 cm² for differential reflectometry and microhardness testing. A few pieces were selected at random and tested on the differential reflectometer for compositional inhomogeneities. This was done by illuminating only one sample in the differential reflectometer. Any inhomogeneities in the sample would produce a non-zero signal in the differential reflectometer output. None could be detected. In Tables 3-1 and 3-2, those alloys used in the compositional modulation and aging experiments are listed, respectively.

Table 3-1. Alloys Used in Composition Modulation Experiments

Cu - 2.7 a/o Co

Cu - 2.5 a/o Co

Cu - 2.0 a/o Co

Cu - 1.5 a/o Co

Cu - 1.0 a/o Co

Cu - 0.5 a/o Co

Pure Cu

Table 3-2. Alloys Used in Aging Experiments

Cu - 2.7 a/o Co

Cu - 2.0 a/o Co

Cu - 1.0 a/o Co

3.3 Differential Reflectometer

The differential reflectometer is a kind of optical spectrometer, the output of which is a normalized difference in reflectivity of two samples as a function of wavelength, $\Delta R/\bar{R}$ vs λ .^{3,4} Originally conceived to experimentally determine the shift in energy of interband transitions that occur upon alloying,^{5,6,7} the differential reflectometer has proven successful in studying long¹¹ and short¹² range ordering, dezincification of alpha brasses,¹³ thickness and formation kinetics of corrosion products,⁷⁸ and in situ studies of the corrosion of Cu and Cu-Ni alloys.⁷⁹

The differential reflectometer has been demonstrated to be very sensitive in detecting small differences in composition. Compositional differences as small as 0.05 a/o have been detected in selected applications.⁸⁰ It was the aim of this work to exploit this capability in order to detect changes in composition of an alloy matrix as precipitation occurred.

A detailed description of the differential reflectometer has been given elsewhere.^{3,4} Only a brief description of its functions will be given here, in conjunction with Figure 3-1.³

The usable output of the xenon light source lies in the range of 200-800 nm. This light enters a double scanning monochromator, which for all experiments in this work,

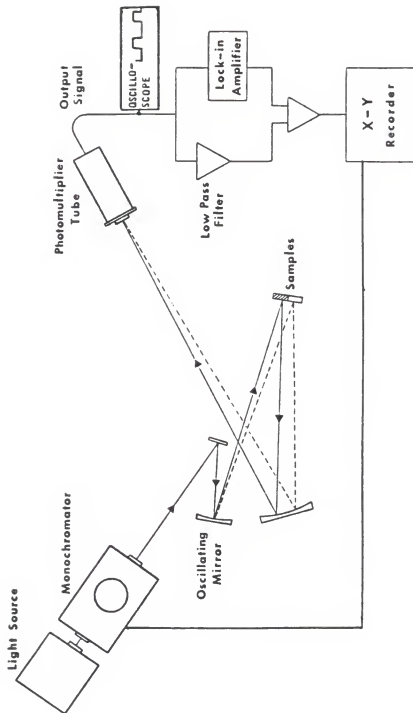


Figure 3-1. Schematic of Differential Reflectometer. (Ref. 3)

was operated at a scan rate of 200 nm/min. After exiting the monochromator, the beam is reflected from a flat mirror to an oscillating mirror which focusses the beam at near normal incidence alternately on each sample. The spot size of the beam on each sample is approximately $2 \times 2 \text{ mm}^2$. Once reflected from the samples, the beam is focussed by a fixed mirror onto a ground plane of fused quartz causing the light to diffuse upon the face of the photomultiplier tube (PMT) to quash any effects caused by the oscillating light beam. The amplified signal of the PMT is divided into two channels, one of which is a low pass filter which yields the average reflectivity, $\bar{R} = (R_1 + R_2)/2$. The other channel contains a lock-in amplifier where the difference in reflectivity, $\Delta R = R_2 - R_1$ is produced. A ratio of these two signals is made and is used as input for the y-axis of an x-y recorder. The x-axis input is connected through a variable resistor to the drive of the monochromator, the result being a spectrum of $\Delta R/\bar{R}$ vs. λ .

In order to maximize the signal, the two samples analyzed in the differential reflectometer must be mounted as close to each other as possible. This is achieved by grinding a flat surface on each sample and holding them together in a thermosetting metallurgical mount. After polishing, the mount is clamped onto a stage in the differential reflectometer. The stage is capable of being moved vertically, by which the beam can be centered, or

horizontally, by which different areas along the juncture of the samples can be studied. In most cases, three such areas were measured.

3.4 Polishing Procedure

Each sample studied in the differential reflectometer was prepared in the following manner.

1. The two specimens -- either of differing composition or differing heat treatment -- were mounted adjacent to each other in a quick setting polymeric material.⁸¹
2. In order to bring the surfaces of both specimens into the same plane, the sample was ground on a grinding wheel using 180 grit paper with filtered kerosene as a lubricant.
3. The sample was then ground by hand using successively finer grits -- 240, 320, 400, 600 -- with filtered kerosene as a lubricant.
4. Final polishing was performed with 1 micron diamond paste on a felt cloth using an oil base lubricant.
5. The sample was then rinsed in methanol, dried in a stream of desiccated air, and taken immediately to the differential reflectometer for measurement.

With the exception that only one specimen needed to be mounted, samples used in the microhardness tests were ground and polished by the same method as above through the diamond polish. In order to reveal the grain structure the samples were swabbed with an etchant composed of 2:1:1 ammonium hydroxide:hydrogen peroxide (3%):water. These

samples were then rinsed in methanol and blown dry and taken immediately to the microhardness tester.

3.5 Aging

Aging temperatures were chosen to reflect a range of precipitation rates from slow to moderately rapid growth. To that end, all three alloy compositions -- Cu-1 a/o Co, Cu-2 a/o Co, and Cu-2.7 a/o Co -- were given aging heat treatments at 400°C, 500°C, and 600°C. In addition, Cu-2.7 a/o Co was aged at 450°C and 550°C.

All samples to be aged were placed in a fused quartz tube which was evacuated with a mechanical pump to a pressure of approximately 0.1 Torr. The pump remained connected to the tube and operated continuously during the aging heat treatment. At the end of the aging heat treatment helium was used to break the vacuum, and the samples were immediately quenched in tap water.

For a specific isothermal aging heat treatment, the aging times were recorded accumulatively. For example, if a given alloy had been aged for fifteen minutes and examined, and the next test required a thirty minute aging heat treatment, the same sample was demounted, aged for fifteen minutes and remounted. In this way any possible error involved in using different samples was avoided.

Upon removal from the furnace, samples aged for six hours or less appeared to be clean and free of contamination.

Samples aged longer than six hours were observed to have a flaky black surface scale. The origin of the scale was probably a combination of oxide and residue from the mechanical pump oil. However, because all samples were of necessity ground and polished subsequent to each aging heat treatment, any contamination resulting from that treatment was removed.

3.6 Microhardness Tests

Diamond pyramid hardness tests (Vickers scale) were conducted upon Cu alloys containing 2.7 a/o, 2.0 a/o, and 1.0 a/o Co. Each of the alloys was given a series of isothermal aging heat treatments at 400°C, 500°C, and 600°C. All samples were subjected to a 500g load applied by the indenter. By maintaining the load at this specified value, no load dependent variations were introduced into the measurements. Although the sample depth probed in a microhardness test is much larger than the sample depth probed by a light beam (approximately 40 μm vs. 0.01 μm), microhardness tests were considered to be a more appropriate alternative than standard hardness tests where the disparity in probe depth would have been far greater.

For each time in the aging sequence of a sample, a set of twenty-five microhardness measurements was made. From these measurements a diamond pyramid hardness number (DPN) was calculated along with the 95% confidence

interval. As was the case with the optical data, a sequence of measurements comprising a set of isothermal heat treatments was carried out on individual samples. Care was taken to remove the damage of the previous measurements caused by the indenter. This was done by grinding well below the level of the indentations made during the previous run.

CHAPTER 4 EXPERIMENTAL RESULTS AND DISCUSSION

4.1 Microhardness Tests: Results and Discussion

Previous experiments on dilute copper-cobalt alloys have established that the changes in hardness which occur during aging heat treatments are caused by the formation of spherical cobalt-rich precipitates. The purpose of performing microhardness measurements for this work was to provide a link from these previous experiments to the optical measurements designed for this work. In this section, results of the microhardness tests will be presented. The results will be seen to be consistent with that which is known to occur during a precipitation reaction. Furthermore, it will be shown that the results of these measurements verify the findings of other researchers who have performed similar measurements.

Microhardness measurements were carried out on alloys containing 2.7 a/o Co, 2.0 a/o Co, and 1.0 a/o Co. These alloys were aged at three different temperatures -- 600°C, 500°C, and 400°C. The results of these measurements can be seen in Figures 4-1 to 4-6.

In Figure 4-1, the diamond pyramid number is plotted versus aging time for alloys containing the three amounts

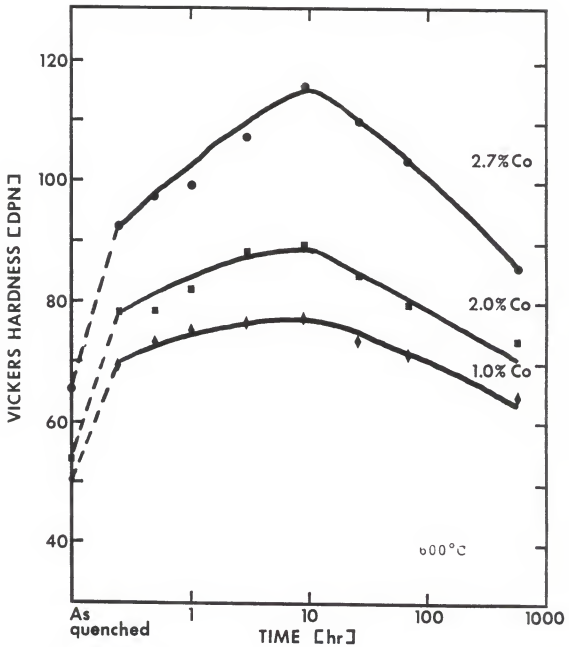


Figure 4-1. Hardness vs Time for Alloys Aged at 600°C .

of cobalt mentioned above and aged at 600°C . For the as quenched alloys the hardness increases with solute content. This proved to be the case in all samples analyzed, and is consistent with the theory of the effect of solute elements on the hardness of solid solutions. Solute atoms have been shown to impede the movement of dislocations by collecting at them and pinning them.^{57,82} As the concentration of solute atoms increases, more dislocations can be pinned, leading to increased hardness.

Figure 4-1 shows that for all alloys which had been aged at 600°C , the hardness increased considerably between the as quenched state and fifteen minutes of aging. After this, the hardness increased steadily, but more moderately, up to its peak value at about nine hours. Past nine hours, the hardness decreased steadily. At all times, the alloy with the greater solute concentration exhibited higher hardness.

Aging each alloy at 500°C produced results indicative of the slower diffusion rate which exists at this lower heat treating temperature. As is seen in Figure 4-2, the increase in hardness from the as quenched state to the first aging time of 15 minutes is much more moderate than in the case of aging at 600°C . The increase was less than half the increase seen at 600°C . In addition, increases tended to be moderate and no peak was reached even after aging for 220 hours, although the values of hardness at 220 hours are higher than the peak values for the alloys

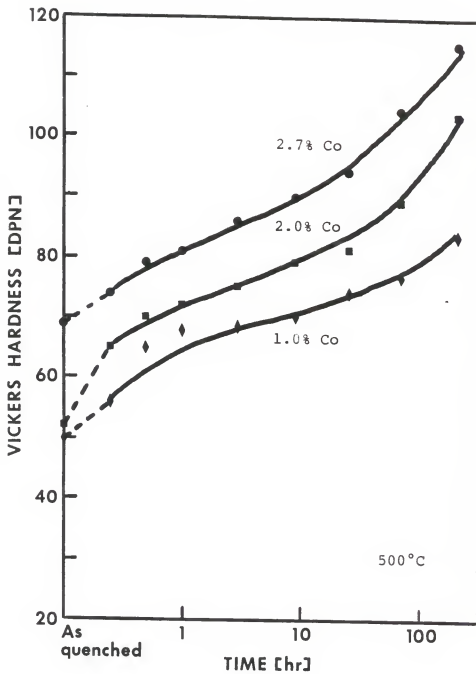


Figure 4-2. Hardness vs Time for Alloys Aged at 500°C.

aged at 600°C. The fact that these values are higher can be accounted for by the lower solubility at 500°C for Co in Cu. At 600°C, the solubility for cobalt is about 0.4% whereas at 500°C, it is less than 0.1%. This decreased solubility leads to a greater volume fraction of precipitate as determined by the phase diagram tie line, which in turn leads to a higher hardness. Again, it can be seen that at each aging time the alloy containing a greater amount of solute possesses a higher hardness.

The results of aging each alloy at 400°C can be seen in Figure 4-3. At 400°C there is only a very slight increase in the hardness for each composition in aging up to 26 hours, indicating that the precipitation reaction has barely begun even after this length of time. The diffusion rate is evidently so slow at this temperature that in terms of aging time several more orders of magnitude of time would be necessary to bring these alloys into a condition of peak hardness. These results did show, however, that room temperature aging would not occur and that therefore it was not necessary to give the sample a solution heat treatment before each aging experiment was performed. This allowed the use of individual samples for a series of aging times thus avoiding the error associated with using different samples. This observation was also made by Witt and Gerold.³⁷

In Figures 4-4 to 4-6 are plotted the diamond pyramid number versus aging time for each composition where aging

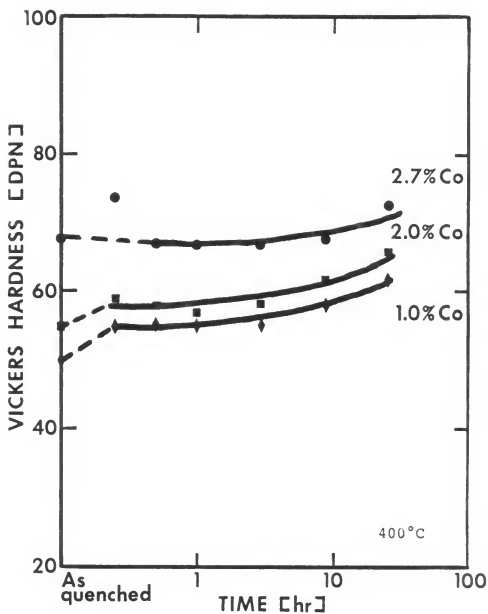


Figure 4-3. Hardness vs Time for Alloys Aged at 400°C.

temperature is the variable parameter. In these figures, the role of aging temperature in influencing the precipitation rate is clearly seen. In Figure 4-4, for example, which shows microhardness data for a Cu-2.7% Co alloy aged at 600°C, 500°C, and 400°C; the increased precipitation rate with increasing temperature is quite evident. Starting from essentially the same hardness in the as quenched state, the alloy aged at 600°C proceeds to reach a peak in microhardness much faster than those alloys aged at 500°C or 400°C. This same pattern is repeated for the Cu-2.0% Co alloys and the Cu-1% Co alloys, seen in Figures 4-5 and 4-6 respectively.

The microhardness data presented here can be seen to represent the type of data that would be found in a typical precipitation reaction. The increase in hardness, although influenced by a number of factors, is principally influenced by the fraction of coherent precipitate. The peak value in the microhardness is indicative of that point where the precipitates have grown to a size that warrants the formation of an interface. This is achieved by the creation of dislocations to accommodate the strain introduced to the lattice by the mismatch between the precipitate and the matrix. The subsequent decrease in hardness past the peak is a manifestation of more and more particles achieving the critical size at which they change from a coherent to incoherent state.

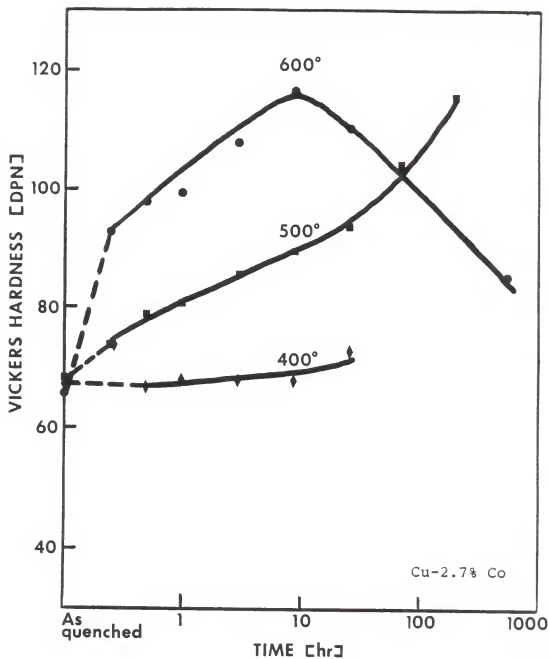


Figure 4-4. Hardness vs Time for Cu-2.7% Co Aged at 600°C, 500°C, and 400°C.

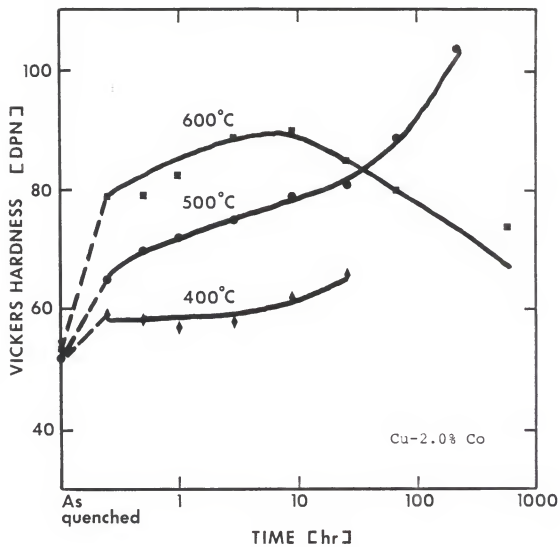


Figure 4-5. Hardness vs Time for Cu-2.0% Co Aged at 600°C, 500°C, and 400°C.

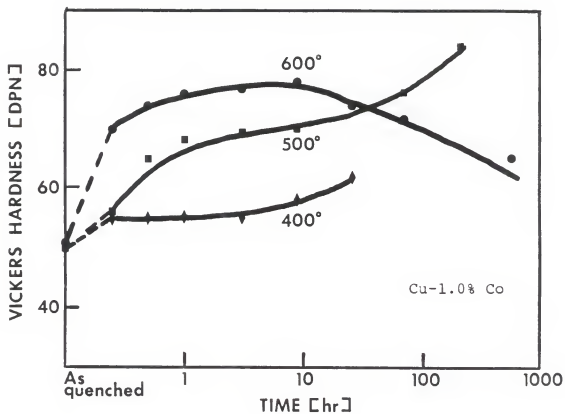


Figure 4-6. Hardness vs Time for Cu-1.0% Co Aged at 600°C, 500°C, and 400°C.

There are various values reported for this critically sized particle in the Cu-Co system, i.e., the size at which the precipitate changes from the coherent to incoherent state. Generally, these values, seen in Table 4-1, fall in the range of 40-100 Å. The only values to fall outside of this range is 175 Å which was reported by Phillips and Livingston³¹ and 120 Å which was reported by Humphreys.³⁵ Both of these values for radii were found using samples which had experienced no deformation after the aging heat treatment. Phillips³³ has also reported the maintenance of coherency up to precipitate radii of 250 Å in the absence of any deformation. However, the application of any deformation to the sample assists in the nucleation of dislocations which provides for the establishment of an interface in changing from a coherent to incoherent state. In the present work, both the use of the indenter in the microhardness tests and the use of the polishing wheel in order to obtain a specular surface for taking optical measurements could provide the deformation necessary to cause an interface to be formed between the precipitate and the matrix. Therefore, the results presented here most likely coincide with a radius of 40-100 Å at peak hardness.

Based upon the data obtained from the microhardness tests and the coincidence of this data with the work of others who have studied precipitation in the copper-cobalt system, the conclusion can be reached that the alloys were

Table 4-1. Radius of Precipitate at Peak Property
for Copper-Cobalt System

	Particle Radius at Peak	Measurement	Ref.
Livingston & Becker	70 Å ^o	Hardness	29
Livingston	70 Å ^o	Yield Stress	30
Phillips	46-75 Å ^o	Hardness	33
Phillips & Livingston	175 Å ^o *	TEM	31
Phillips	50 Å ^o	Yield Stress	34
Humphreys	120 Å ^o	TEM	35
Threadgill & Wilshire	40-75 Å ^o	Creep	43
Amin, Gerold & Kralik	100 Å ^o	Hardness	44
Wilhelm	70 Å ^o	Not Specified	46
Tautzenburger & Gerold	40 Å ^o	Creep	48

* Sample Undeformed

heat treated properly to produce a precipitation reaction. Furthermore, the results indicate that the goal of observing precipitation in regions of relatively rapid, moderate, and slow growth has been achieved.

Among the researchers who have studied this system, there is little disagreement as to the nature of the precipitation reaction. It is generally conceded that the precipitate is spherical, face-centered cubic, and remains coherent with the lattice until it achieves a size of approximately 40-100 Å. There has been nothing found so far in this work to contradict these findings.

4.2 Compositional Modulation: Results and Discussion

As has been discussed in Chapter 2, the optical properties of copper alloys have been found to be strongly dependent on composition. In the case of copper with multivalent solutes, a linear shift of the threshold electronic transition at 2.2 eV to higher energies was found as the average solute concentration was increased above one percent.⁵ In the case of copper-nickel alloys, however, there was no composition dependence seen in the energy of the threshold transition.⁷ Additions of up to 24% nickel produced no change in this transition energy. The demonstration of this phenomenon by both differential reflectometry⁷ and photoelectron spectroscopy⁶³ was offered as confirmation of the virtual-bound-state model of Friedel⁶⁷ and

Anderson,⁶⁸ who had predicted this type of behavior for copper-nickel alloys.

The purpose of performing compositional modulation experiments for this work was twofold. Firstly, it was necessary to determine the manner in which cobalt would affect the optical properties of copper. To do this, "traditional" compositional modulation experiments were performed, in which the optical properties of the average compositions of the two samples were investigated. The design and results of these experiments are discussed below. Because cobalt and nickel lie next to each other in the periodic table and because they both derive their ferromagnetism from spin imbalance of their unfilled d-bands,⁸³ the results of these experiments on Cu-Co alloys are compared to previous research on the optical properties of Cu-Ni alloys. Particular attention is made to the virtual-bound-state model.

Secondly, another type of compositional modulation experiment on Cu-Co alloys was performed. In this investigation, the difference in solute concentration between the two samples studied is the variable parameter. The design and the results of these compositional modulation experiments will be discussed in the second half of this section. In particular, the relationship between these experiments and the optical properties of aged alloys will be considered.

In Figure 4-7, differential reflectograms for average sample compositions of Cu-1.5% Ni and Cu-1.5% Co are presented. In this figure, an almost identical pattern in optical response is evident. The features of the copper-nickel differential reflectogram have already been described by Hummel.⁸⁴ The structure from "a" to "b" is caused by interband transitions at the threshold energy of 2.2 eV. The maximum designated "d" is a manifestation of transitions from the lower d-bands of copper to the Fermi energy. Finally, the broad structure at "c" has been ascribed to electronic transitions involving the d-bands of nickel. The similarity between these two reflectograms represents a new type of pattern seen in differential reflectograms. Previous work on copper with multivalent solutes revealed that all differential reflectograms of this alloy group had a common pattern. The evidence here suggests that there will be one pattern for all differential reflectograms of copper-transition metal alloys.

The study of the effect of cobalt composition on the electronic structure of copper was then broadened. These compositional modulation experiments were conducted by changing the average composition of the two samples studied by differential reflectometry. (It has been shown¹¹ that the transition energies measured by differential reflectometry are the equivalent of the transition energies for an alloy whose composition is the average of the composition of the two alloys measured, provided that the difference in

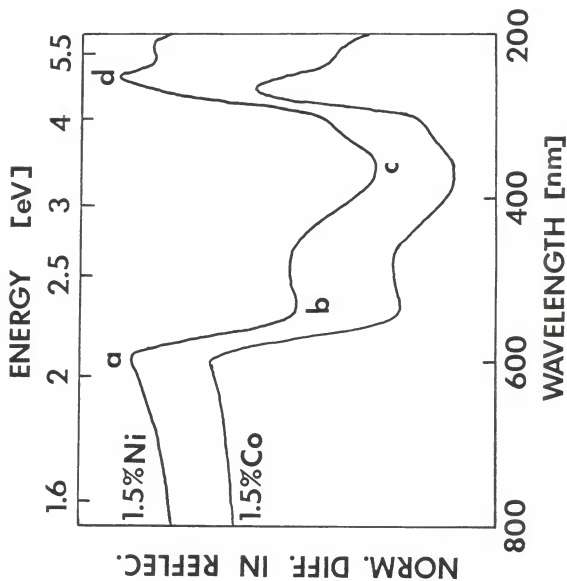


Figure 4-7. Differential Reflectograms of Cu-1.5% Ni (Ref. 84) and Cu-1.5% Co. (Compositions indicate average solute content of the two samples used.)

composition is small.) Although somewhat hampered by the limited solubility for cobalt in copper, this research did provide a measure of compositional dependence up to about 2.4% Co. In Figure 4-8, differential reflectograms are shown for average compositions of Cu-0.5% Co, Cu-1.5% Co, and Cu-2.4% Co. To obtain these average compositions the following pairs of samples were examined: pure Cu and Cu-1% Co, Cu-1% Co and Cu-2% Co, and Cu-2% Co and Cu-2.7% Co.

As in the case of nickel, there was no shift seen in the transition energy as the composition was changed. As has been discussed, the reason for this composition independence of the threshold transition energy has been accounted for by the virtual-bound-state model of Friedel⁶⁷ and Anderson.⁶⁸ Their contention that the nickel electrons maintain highly localized levels around nickel atoms when alloyed with copper, seems to extend to cobalt impurity atoms as well.

Peak "d", which is caused by transitions from the lower d-bands of copper to the Fermi energy, does show a very small composition dependence. It can be seen that this peak shifts to slightly higher energies as the amount of cobalt is increased. This same shift toward higher energies with increasing solute content has also been observed in copper-nickel alloys.⁷ The minimum designated "c" in these differential reflectograms, although seen in Figure 4-8 to shift toward higher energies as cobalt content was increased showed no strict composition dependence in other

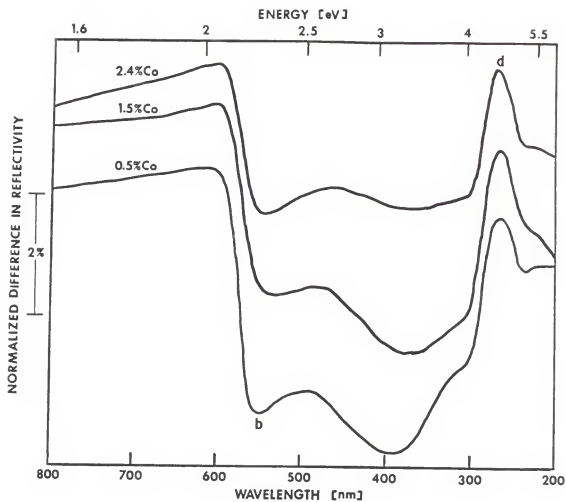


Figure 4-8. Differential Reflectograms of Various Copper-Cobalt Alloys. (Compositions indicate average cobalt content of the two samples used.)

differential reflectograms. In copper-nickel alloys, this minimum is thought to be caused by nickel electronic transitions, but cobalt has been found to have no strong optical transitions in this energy range.^{75,77,85}

As has been established, a precipitation reaction is defined to be the decomposition of a metastable solid solution in which a second phase nucleates, grows, and coarsens, and in which the matrix is necessarily depleted of solute in order that the second phase be produced. So far, this work has established the conditions under which a precipitation reaction can be produced, and has verified the presence of a second phase by means of microhardness measurements. However, measurements of mechanical properties, such as the microhardness of an alloy, only yield information about the state of the precipitate, for example, whether or not coherency has been maintained. While this is, of course, useful, no information has been obtained about the extent to which the decomposition has progressed. There is no metallurgical law which establishes a link between the hardness of an alloy and the volume fraction of precipitate, or conversely, the composition of the matrix.

It has been seen that the optical properties of an alloy are very strongly dependent upon its composition (See Section 2.3), and therefore, their measurement should be a candidate for a method of determining the changes in composition which occur in the matrix during a precipitation reaction. Finnegan¹³ has already shown the utility of

making optical measurements, specifically differential reflectometry, in determining the extent of dezincification in alpha brasses when they are subjected to various corrosive environments. Although in the case of dezincification, the alloy experiences an actual loss of solute, a precipitation reaction can be viewed in a similar manner, for the reason that the solute is removed from the matrix by the formation of the second phase.

It has been demonstrated that the optical properties of copper-cobalt alloys parallel those of copper-nickel alloys, and that these findings indicate that copper-cobalt alloys behave according to the virtual-bound-state model. Using Figure 4-8, it has been shown that Co additions do not affect the energy of the copper threshold transition at 2.2 eV, as in the case of multivalent solute additions. Because the differential reflectometer yields information about the alloy composition which is the average of the two samples investigated and because no shift in transition energy occurs as the average alloy composition was changed, an alternative method for determining the effect of cobalt additions on the optical properties of copper was chosen. The average of the composition of the two samples was replaced by the difference in the composition of the two samples.

In this second type of compositional modulation, experiments were conducted in a manner so as to simulate the aging experiments which are described in the next section.

Specifically, in these experiments, the solute composition of one sample was held constant while the solute composition of the samples measured against it was successively decreased. In this way, the difference in solute content between the two samples was made the independent variable. All of the samples used in these experiments were given solution heat treatments in order that there was no precipitate present, therefore, the results would be indicative of composition effects only. The results of these experiments can be seen in Figures 4-9 to 4-11.

In Figure 4-9, a Cu-2.7% Co alloy was measured against copper alloys containing 2.5% Co, 2.0% Co, 1.5% Co, 1.0% Co, and 0.5% Co. The shape of these curves can be seen to be similar to those curves described in the first part of this section, where the effect of cobalt upon the electron band structure of copper was discussed. Qualitatively, it is immediately apparent that as the difference in solute composition of the two samples is increased that the signal strength of the spectra is also increased. In order to attempt to quantify this increase in the signal strength, two features of the spectra, which are present in all spectra and which lend themselves to measurement (the minimum formed between approximately 600-550 nm and the maximum at 270 nm), were examined. These two features are the results of changes in strength of the two most prominent valence transitions in copper, specifically the threshold transitions at 2.2 eV and the L_2 - L_1 transition at 4.5 eV (See

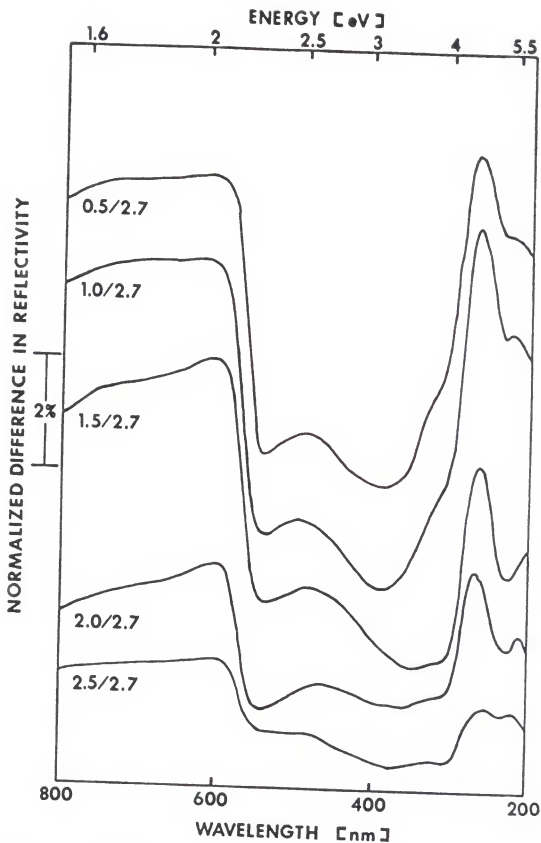


Figure 4-9. Differential Reflectograms of Cu-2.7% Co versus Cu-0.5% Co, Cu-1.0% Co, Cu-1.5% Co, Cu-2.0% Co, and Cu-2.5% Co.

Section 2.3). Because of the absence of a reference point from which the peak at 270 nm could be measured, the change in the differential reflectivity between 600-550 nm was chosen as the basis upon which the signal strength was measured. Of note is the fact that even when the difference in the solute content is only 0.2% (bottom curve of Figure 4-9), the change in the differential reflectivity at the threshold transition is slightly more than 0.5%. This demonstrates the utility of performing optical measurements in determining small differences in composition. It is apparent that differences in composition at least as small as 0.1% can easily be detected.

In Figures 4-10 and 4-11 are seen the spectra showing Cu-2.0% Co and Cu-1.0% Co compared against samples of lesser cobalt content. It is again apparent in these figures that as the difference in solute content in the two samples is increased that the signal strength of the spectra is increased. Furthermore, the relationship between the difference in solute content and the signal strength in all three sets of experiments depicted in these figures was found to be the same. By using this observation and by plotting the signal strength at the threshold transition as a function of the difference in solute content, the calibration curve shown in Figure 4-12 was produced. As is evident, a linear relationship was found to exist between the percent change in differential reflectivity (signal

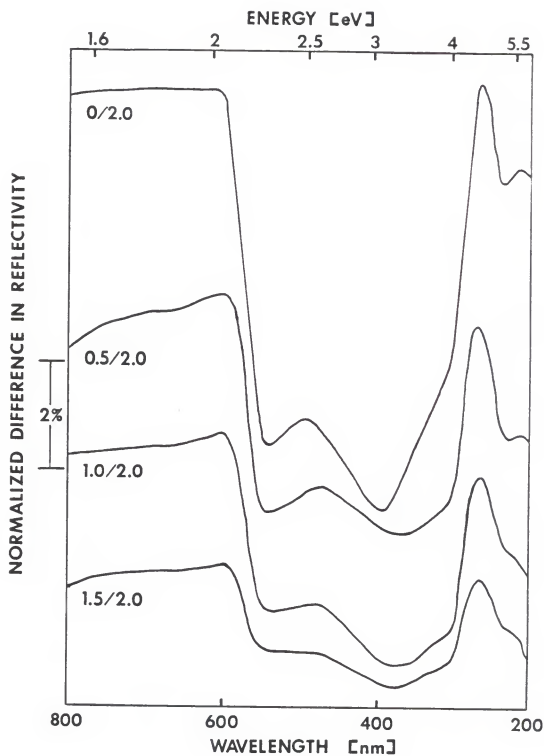


Figure 4-10. Differential Reflectograms of Cu-2.0% Co versus Pure Copper, Cu-0.5% Co, Cu-1.0% Co, and Cu-1.5% Co.

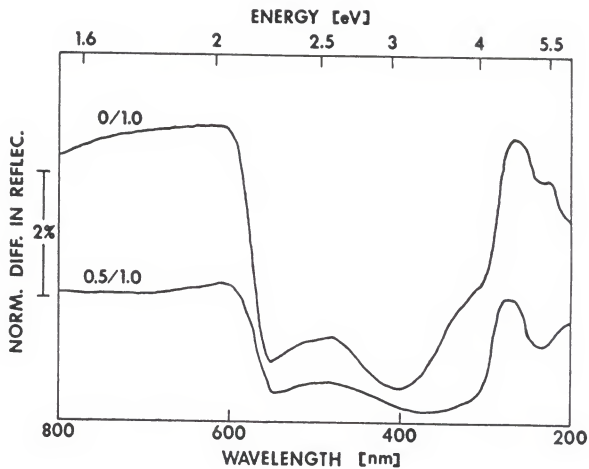


Figure 4-11. Differential Reflectograms of Cu-1% Co versus Pure Copper and Cu-0.5% Co.

strength) and the difference in solute content. The slope of the line is approximately $3\%/\Delta C$.

This relationship between signal strength and the difference in composition between the two samples measured is an observation which has been previously unexploited in differential reflectometry. The reason for this lies in the nature of the solute element, which in this case is a transition metal. As has previously been discussed (see Section 2.3), when copper is alloyed with multivalent solutes, such as zinc, the energy of the electronic transitions shifts as a function of solute content. By measuring the change in the energy of these transitions by differential reflectometry, it has been possible to determine the solute content of unknown alloys. This was the method which was used by Finnegan et al.¹³ to determine the extent of de-zincification in alpha brasses. For the reason that cobalt is a virtual-bound-state element in copper, and hence no shift in energy of the electronic transition occurs, the composition dependence of the signal strength must be used to determine the composition of an unknown alloy.

This relationship between the differential reflectivity and the solute composition of a transition metal in copper has been experimentally observed by other researchers.^{63,69} It can qualitatively be seen in Figure 2-10, which shows reflectivity data for pure copper, Cu-13% Ni, and Cu-23% Ni.⁶³ The reduction of the reflectivity for the alloyed samples in the energy region preceding the drop in

reflectivity at the threshold can be seen to be approximately linear. This combined with the fact that the reflectivity of all samples crosses at approximately the same value would yield a differential reflectivity change that was linear with the difference in solute content.

More quantitatively, Beaglehole and Kunz⁶⁹ in measuring differential reflectivity of dilute copper-nickel alloys found that this quantity changed directly as a function of the difference in solute composition at 628 nm. Although no measurements of the optical properties of copper-cobalt alloys have been performed by other researchers, it has been shown that cobalt^{85,86} and nickel^{63-66,70} are both virtual-bound-state elements in copper. This fact, combined with their similar electronic structure and position in the periodic table, makes the determination that they display a similar influence upon the optical properties of copper alloys seem quite reasonable.

The utility of the calibration curve in Figure 4-12 as it applies to a precipitation reaction can be demonstrated in the following example. If two samples of known solute content, one of which has been solution heat treated and the other of which has been solution heat treated and aged, are measured by differential reflectometry, the difference in the matrix solute content between the two samples can be obtained by determining the signal strength of the resulting spectrum. This yields a measure of the extent to which the precipitation reaction has progressed. The

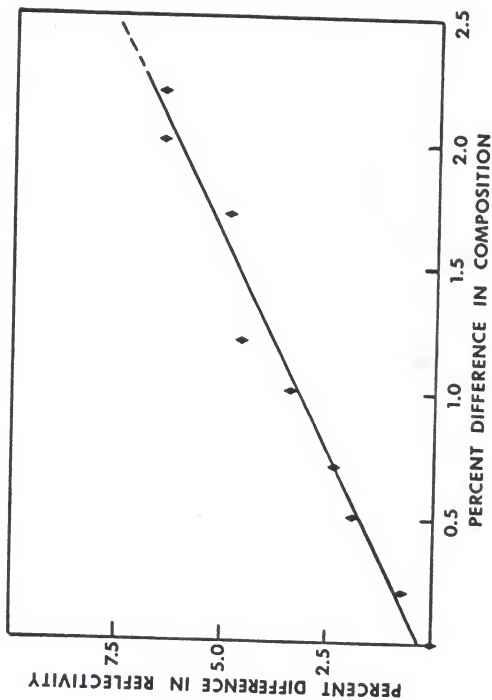


Figure 4-12. Signal Strength ($\Delta R/\bar{R}$) versus Difference in Cobalt Concentration.

utility of differential reflectometry in determining the depletion of solute from the matrix during precipitation will be discussed in the following section.

4.3 Aging Experiments

In the preceding section, experimental data describing the relationship between the composition of Cu-Co alloys and the optical properties of these alloys was presented. It was also demonstrated that differential reflectometry provides a method by which the cobalt concentration of an unknown Cu-Co alloy can be determined provided that a reference sample of known solute concentration is available. In this section, the utility of differential reflectometry in following a precipitation reaction by tracking the associated matrix depletion of solute will be explored. In addition, any additional optical effects that occur during the precipitation reaction that are not based solely upon composition differences will be acknowledged.

In these experiments three alloys of varying cobalt content were studied -- Cu-2.7% Co, Cu-2.0% Co, and Cu-1.0% Co. Each alloy was aged at 600°C, 500°C, and 400°C. In addition, the Cu-2.7% Co alloy was aged at 550°C and 450°C.

In order to determine the kinetics of the solute depletion during precipitation, differential reflectometry was performed on samples that were identical in initial solute composition, but differed in subsequent heat treatment. In

these experiments, both samples were given solution heat treatments. One of the samples was then additionally aged at a specific temperature for a series of times. Differential reflectometry spectra were obtained to record the difference in optical properties between the two samples as a result of the aging regime.

Figure 4-13 shows a typical differential reflectogram from these experiments. The two samples used to obtain this spectrum were both Cu-2.0% Co. One sample was solution heat treated while the other was solution heat treated and aged at 600°C for one hour. The two most prominent features of this spectrum are a minimum formed between 600 nm and 550 nm and a maximum occurring at 280 nm. These features appear at the same wavelengths as those described in the previous section during the compositional modulation experiments. On the basis of the signal strengths of the minima centered at 550 nm, the difference in composition between the two samples is approximately 0.5% Co. It was also determined that the aged sample was the sample which contained the lesser amount of matrix solute. This finding is interpreted to be the fundamental result of a precipitation reaction, in which cobalt is removed from the matrix in order that cobalt-rich precipitates can be formed.

In Figure 4-14 a series of differential reflectograms for a Cu-2.0% Co alloy are displayed. Again, one sample was solution heat treated while the other was solution heat treated and then aged. Figure 4-14 shows the spectra for

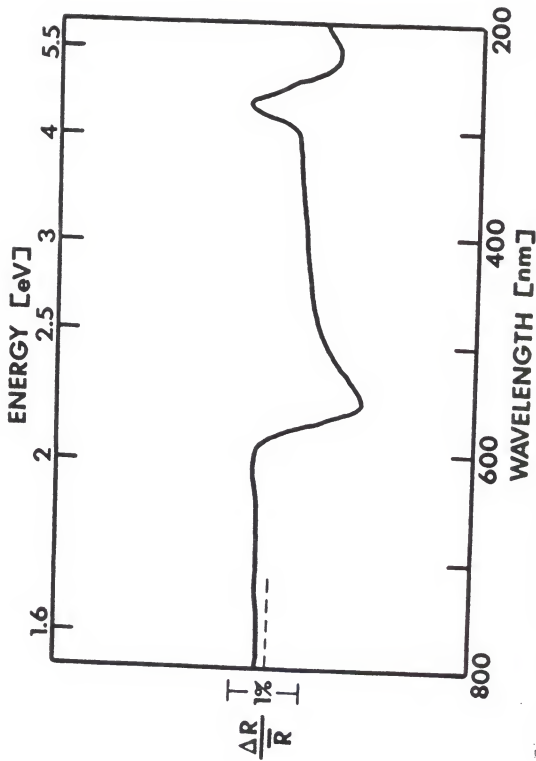


Figure 4-13. Differential Reflectogram of a Cu-2.0% Co Alloy. (One Sample was Solution Heat Treated and Aged for One Hour at 600°C, the Other sample was Solution Heat Treated.)

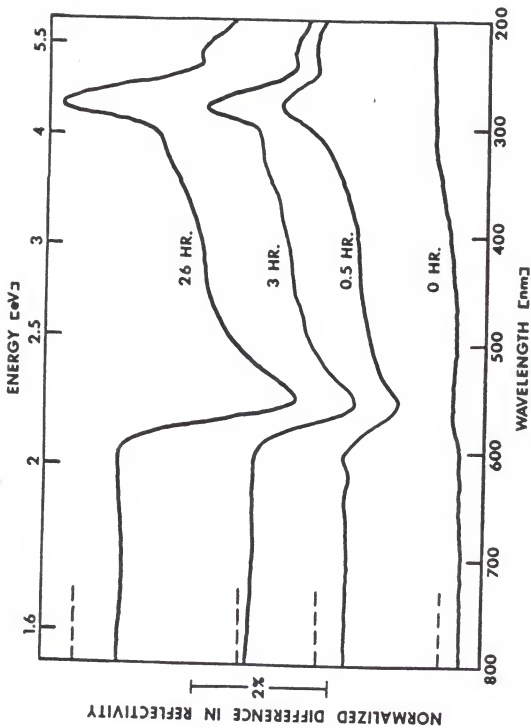


Figure 4-14. Differential Reflectograms of the Aging Sequence of a Cu-2.0% Co Alloy Aged at 600°C.

0.5 hr, 3.0 hr, and 26.0 hr of aging. The 0 hr spectrum depicts two samples that were identically solution heat treated. The lack of any clearly defined structure in this spectrum shows that the samples started in an identical condition. In response to the aging heat treatments given to the one sample, however, the spectra indicate that the composition difference between the two samples increased with aging time due to the decreased solute concentration in the aged sample. In the spectra in Figure 4-14, the signal strength indicates that after 26 hours of aging the matrix solute content has been reduced by approximately one percent.

In order to determine the effects of aging time, aging temperature, and solute concentration on the optical properties of these alloys during a precipitation reaction, the signal strength at the threshold transition was plotted as a function of aging time. The results are shown in Figures 4-15 to 4-20. In all cases the first differential reflectogram taken was of two solution heat treated samples, to verify that the samples were identical in the initial condition. A featureless differential reflectogram was expected and was obtained in all cases.

Figure 4-15 shows the change in threshold transition magnitude for the various solute compositions of samples aged at 600°C. As seen in Figure 4-15, the signal strength caused by the samples' composition difference immediately increases after the first aging heat treatment of fifteen

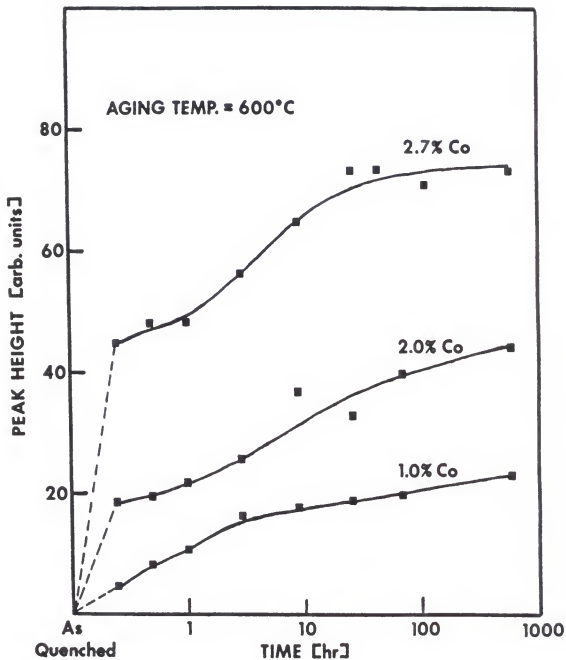


Figure 4-15. Peak Height vs Time for Various Copper-Cobalt Alloys Aged at 600°C .

minutes. In addition, the size of the initial rise in signal strength increases with solute content. After this initial rise, the signal strength increases monotonically for all compositions. For all other compositions and aging times, the signal strength is largest for the alloy containing the most solute. Because signal strength is directly related to difference in solute content, these data indicate that the alloy containing the greatest amount of solute is losing the greatest amount of solute during aging. This is consistent with the gradient-driven mechanism of precipitation.

At the conclusion of the reaction, the matrix solute content will be the limit of solubility for cobalt in copper (about 0.4% Co at 600°C). This value is the same for all initial solute compositions. Therefore, alloys with higher initial solute concentrations must reject more solute than alloys having lower initial solute concentrations in order to reach the solubility limit. Consequently, the disparity in matrix solute content between a solution heat treated and aged sample and one which has been solution heat treated only will be larger in an alloy that has higher solute concentration.

This pattern of finding larger signal strength for larger solute concentration is also seen in Figure 4-16, where the signal strength as a function of time is plotted for each of the three compositions aged at 500°C. Again, the signal strength increases monotonically for all compositions,

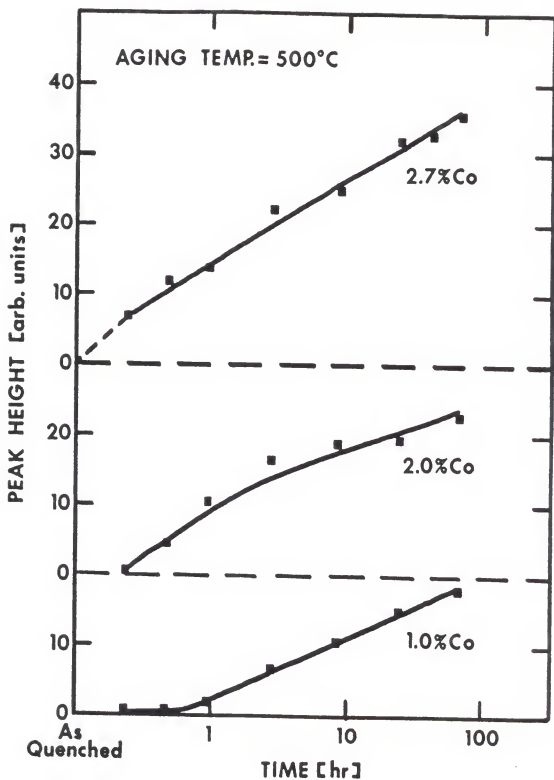


Figure 4-16. Peak Height vs Time for Various Copper-Cobalt Alloys Aged at 500°C.

although more moderately than those samples aged at 600°C . These monotonic increases in the signal strength are an indication that as the aging heat treatment continues, the matrix solute content of the aged samples is continuously diminishing as solute atoms are used to form precipitates.

Figure 4-17 shows the data for the alloys when aged at 400°C . It should be noted that even after 70 hours of aging there is only a slight increase in the signal strength. This, of course, means that precipitation is slow and that the matrix solute concentration in the aged alloys does not change significantly during these heat treatments due to precipitation at this temperature.

In Figures 4-18 to 4-20 signal strength is plotted as a function of time in graphs which show more clearly the effect of temperature. Figure 4-18 shows data for Cu-2.7% Co aged at 600°C , 550°C , 500°C , 450°C , and 400°C . To be noted is the very large initial increase in signal strength for the alloy at 600°C , indicating that at this temperature the precipitation is well under way after 15 minutes aging. In temperature regimes where precipitation is controlled by diffusion, it is expected that the precipitation reaction will proceed at a faster rate when a higher aging temperature is employed. As has been previously stated, the signal strength is proportional to the difference in the matrix solute concentration between the aged and the solution heat treated samples. For this reason it can be seen that the disparity in matrix solute content between the

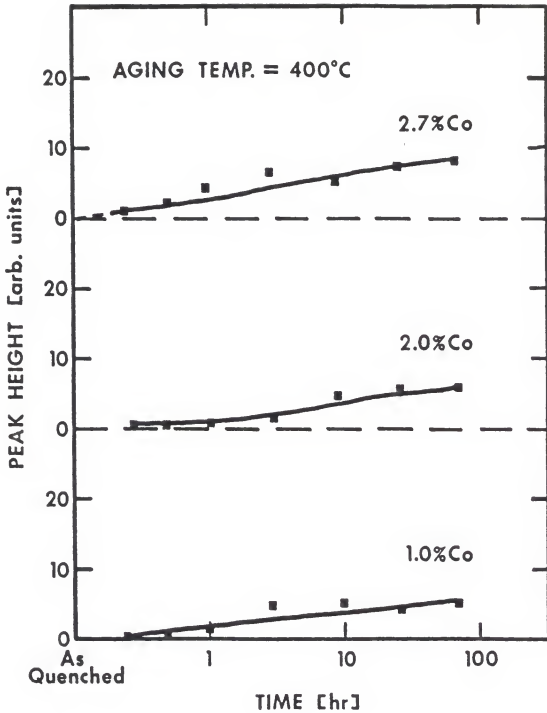


Figure 4-17. Peak Height vs Time for Various Copper-Cobalt Alloys Aged at 400°C.

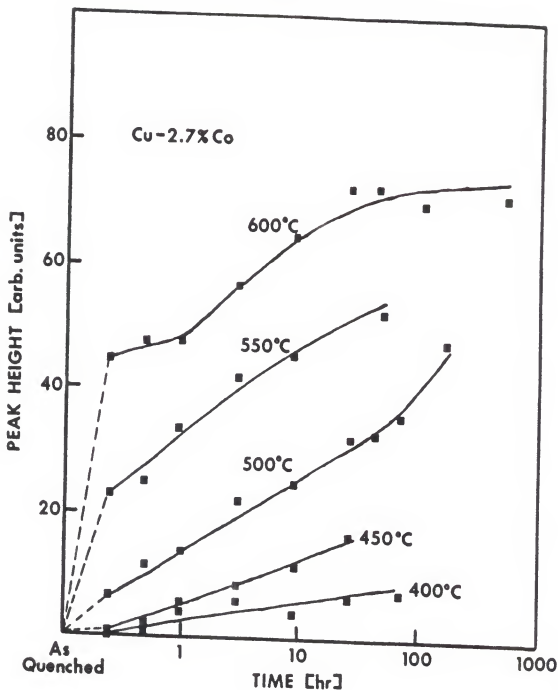


Figure 4-18. Peak Height vs Time for Cu-2.7% Co at Various Aging Temperatures.

aged and unaged samples increases as aging temperature increases.

This same pattern manifests itself for Cu-2.0% Co and Cu-1.0% Co alloys, the data for which can be seen in Figures 4-19 and 4-20, respectively. Here, again, the signal strength is at all times larger as the aging temperature is increased. It is evident, however, that the magnitude of the signal strength decreases as the solute concentration of the alloys decreases.

Finally, the differential reflectograms were examined for effects, other than those related to straightforward compositional differences, which could be caused by the cobalt-rich precipitates. Two such effects were apparent and are discussed in detail below. Firstly, there was a change in shape of the spectra involving the feature designated "c" in Figure 4-7. Secondly, based on the assumption that the alloys were fully aged at 600°C and that therefore the differences in matrix solute content could be determined from the equilibrium solute concentration for each alloy concentration, the signal strength was found to be suppressed when compared with data obtained from compositional modulation. The results of this suppression can be seen in Figure 4-21, where the lower curve was constructed in the following way. Because the equilibrium solute concentration for cobalt in copper is 0.4% Co, the difference in matrix solute concentration between a fully aged 2.7% Co alloy and a solution heat treated alloy is 2.3% Co (point "a" on the graph).

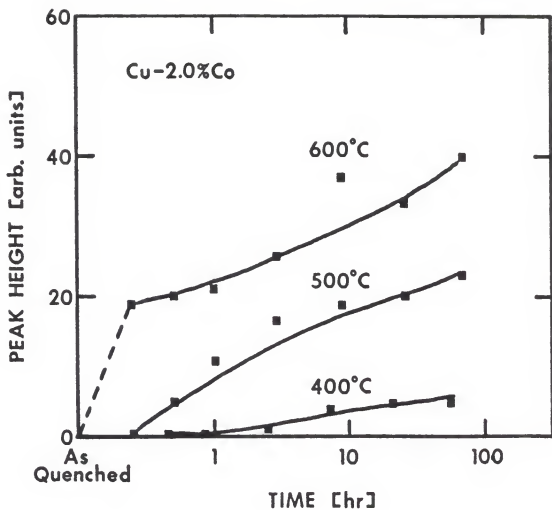


Figure 4-19. Peak Height vs Time for Cu-2.0% Co at Various Aging Temperatures.

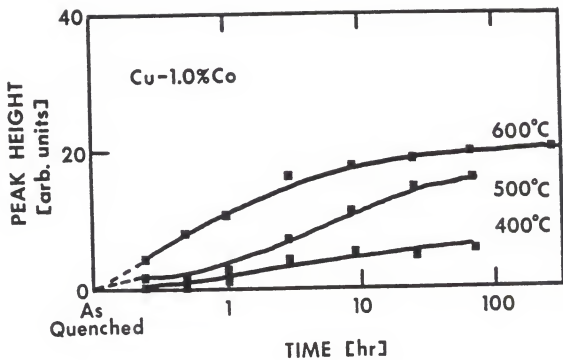


Figure 4-20. Peak Height vs Time for Cu-1.0% Co at Various Aging Temperatures.

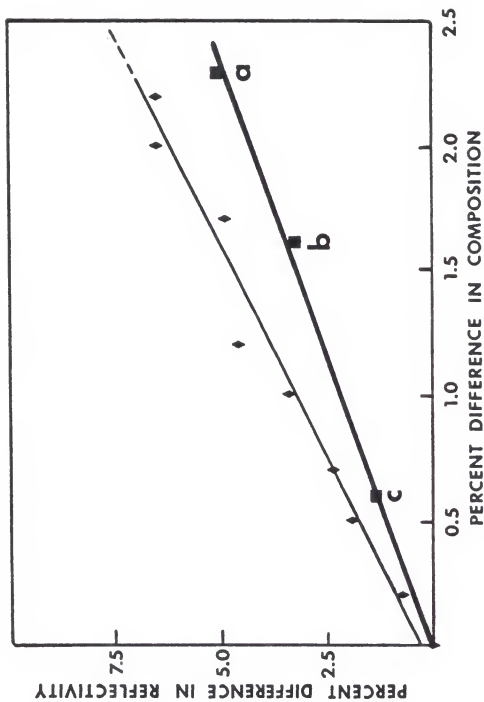


Figure 4-21. Signal Strength vs Difference in Cobalt Concentration for Solution Heat Treated Samples (Top Curve) and Aged Samples (Bottom Curve).

For Cu-2.0% Co the difference is 1.6% Co (point "b") and for Cu-1.0% Co the difference is 0.6% Co (point "c"). This suppression of the signal strength is attributed to the influence of the precipitates on the optical properties of those alloys.

The question arises whether or not the second calibration curve (lower line in Figure 4-21) is a reasonable interpretation of the data obtained from the optical measurements of the aged alloys.

It is necessary to recall that the upper line in Figure 4-21 was obtained by measuring the signal strength at 2.2 eV caused by the difference in solid solution solute concentration between the two alloys. In performing the optical measurements on precipitation heat treated alloys, two alloys of identical solute concentration were measured by differential reflectometry. One alloy was solution heat treated and the other alloy was solution heat treated and aged. As discussed above, when alloys of three different solute concentrations -- Cu-2.7% Co, Cu-2.0% Co, and Cu-1.0% Co -- were aged and measured by differential reflectometry in the manner mentioned above, an increase in the signal strength at the 2.2 eV electronic transition was noted. This was ascribed to a depletion in the matrix solute concentration in the aged alloys which accompanied the formation of a second phase. When the signal strength of the differential reflectograms was compared to the calibration curve obtained from samples that differed in solid solution solute

concentration alone (upper line in Figure 4-21) analysis revealed that the matrix solute concentration for the alloys aged for 590 hours at 600°C was as follows: the Cu-2.7% Co alloy had a matrix solute concentration of 1.1% Co; the Cu-2.0% Co alloy had a matrix solute concentration of 0.9% Co; and the Cu-1.0% Co alloy had a matrix solute concentration of 0.6% Co. The equilibrium solute concentration at 600°C for cobalt in copper has been given as 0.4% Co. It is apparent from this analysis that none of these alloys has reached the equilibrium solute concentration after being aged at 600°C for 590 hours. This might be due to one or more of the following reasons: the value of the equilibrium concentration is not 0.4% Co, but some other value; the precipitation is not complete; there is a capillarity shift of the equilibrium concentration due to a finely divided precipitate structure in this system; the observed solute depletion of the matrix is due to selective oxidation of cobalt during the aging heat treatment; the electronic properties of the matrix and the precipitates are not completely without interaction and the precipitates may play a role in the signal strength at 2.2 eV.

The proposal that the equilibrium solute concentration is not 0.4% Co is probably not valid. Four independent investigations^{30,38,88,89} using two different techniques have established 0.4% Co as the equilibrium solute concentration for cobalt in copper. Furthermore, if one makes the assumption that 0.4% Co is not the equilibrium solute concentration

and the alloys investigated in this work are fully aged, the conclusion would have to be reached that there is a different equilibrium solute concentration for each composition. This conclusion can not be supported by any principle of materials science.

One last possibility exists when considering this matter. It may be that the Cu-1.0% Co alloy has reached equilibrium, but the other two compositions have not. Analysis of Figure 4-15 shows that there is little or no change in the signal strength at 2.2 eV between 26 hours and 590 hours of aging for both of the remaining compositions. Furthermore, as stated above, analysis of the matrix solute concentration of these alloys would indicate values of approximately 1% Co after 590 hours. Clearly, a concentration gradient should exist to drive the reaction toward completion. In the case of Cu-1.0% Co, this gradient could be seen to have driven the reaction to completion in 15-25 hours. It is inconsistent to state that the reaction for Cu-1.0% Co proceeds fairly rapidly, but when the Cu-2.0% Co and Cu-2.7% Co alloys reach a solute concentration of 1.0% cobalt that the reaction proceeds very slowly, if at all.

This last observation begins to address the question of whether or not the data can be interpreted as indicating that the reaction is not entirely complete after aging for 590 hours at 600°C. There are numerous observations reported in the literature that this system can be brought into equilibrium.^{16,30,37,38,88,89} Furthermore, in general,

independent research efforts support the conclusion that the reaction at 600°C brings the system into equilibrium in a range of times from several minutes to several hours.^{16,30, 37,38} The observation that the signal strengths shown in Figure 4-15 can be interpreted as showing no further increase after 26 hours of aging is consistent with the viewpoint that the system has been brought into equilibrium by the precipitation reaction.

As can be seen in Table 4-1, the precipitates that form in this system are quite fine. This requires that some consideration be given to a possible shift toward higher solute concentrations of the equilibrium solute concentration due to capillarity. The magnitude of the capillarity shift is inversely proportional to the radius of the precipitate, so that in a finely divided system, the shift can be significant. However, there are two considerations which argue against any strong effects due to capillarity in this system. Firstly, Witt and Gerold³⁷ have performed aging experiments at 600°C on a Cu-0.6% Co alloy and have reported that precipitates are formed. This would not be possible if there were a significant capillarity shift. Secondly, and perhaps more significantly, assuming that the experimental value given by Servi and Turnbull³⁸ for the surface energy of 190 ergs/cm² for the precipitate-matrix interface is valid, the capillarity shift for precipitates having a radius of 10 nm can be calculated to be only 3% of the equilibrium solute concentration. That is, for precipitates of this size, the

equilibrium solute concentration is shifted from 0.4% Co to slightly above 0.41% Co. This small shift of the equilibrium solute concentration would not significantly affect the results of this work.

The question now arises whether or not the aging heat treatments may have influenced the cobalt concentration in these alloys by a selective oxidation mechanism in which cobalt was removed from the alloy during the heat treatments thereby producing alloys depleted of cobalt. This mechanism could account for the observed increase in signal strength at 2.2 eV in the differential reflectograms by leaving a zone near the surface of the alloys which was depleted of cobalt. Because light penetrates approximately the first 10 nm of the surface of a metallic alloy, this effect could be important. It must be recalled, however, that these alloys were polished after the aging heat treatments. This polishing removed at least 100 microns from the surface of the alloys. In this case, the question becomes whether or not a depleted zone from the selective oxidation of cobalt could extend to a depth of 100 microns or more. Using an activation energy for the diffusion of cobalt in copper of 54,100 cal/mole,⁹⁰ a diffusion coefficient of $1.93 \text{ cm}^2/\text{sec}$,⁹⁰ and a growth factor of 1.38 a diffusion distance on the order of one micron was calculated for an aging temperature of 600°C for 100 hours. This distance can be seen to be much smaller than the depth to which these alloys were

polished. It is therefore unlikely that the signal strength of the optical measurements was influenced by a selective oxidation mechanism.

On the basis of these arguments, the conclusion can be reached that the observed signal strength at 2.2 eV for alloys aged at 600°C is the product of a precipitation reaction, which after 590 hours of aging has been completed. Furthermore, it is evident that the equilibrium solute concentration has been reached. Therefore, for alloys of all compositions aged at 600°C, the matrix solute concentration after 590 hours of aging should be 0.4% Co. It must be recalled how the optical measurements on the aged samples were carried out. An alloy, which was aged, was measured by differential reflectometry against an alloy which contained the identical solute concentration, but in solid solution. Therefore, the difference in solid solution solute concentration between these two alloys can be assumed to be known. Because this difference is the independent variable on the calibration curve of Figure 4-21, the lower curve of this figure was constructed.

It must also be recalled that the difference between the two curves shown in Figure 4-21 is that the upper curve was produced from data taken from alloys which differed by a known solid solution solute concentration only, whereas the lower curve was produced from data taken from alloys which differed by a known solid solution solute concentration and in which one of the alloys contained precipitates. It is,

therefore, concluded that the suppression of the signal strength at 2.2 eV is due to the presence of precipitates in the aged alloys.

However, there is no direct evidence that this suppression of the signal strength is due to the precipitates. The remainder of this section will be devoted to an evaluation of the data that indicates that the precipitates influence the optical properties of these alloys. Although the evidence is indirect, it will provide a basis for future experiments. These experiments will be discussed at the end of the section.

It is evident from Figure 4-21 that the amount of the suppression of the signal strength at 2.2 eV is dependent on the volume fraction of precipitate present. Specifically, the present volume of precipitate phase for a fully aged Cu-2.7% Co alloy is 2.6%, for a fully aged Cu-2.0% Co alloy is 1.8%, and for a fully aged Cu-1.0% Co alloy is 0.7%. This is consistent with precipitation theory. If the precipitates influence the optical properties of these alloys, then the alloy containing the greatest volume fraction of precipitates should show the greatest effect on its optical properties.

However, it can be argued that the magnitude of the suppression of the signal strength at 2.2 eV is too large to be due to the precipitates alone. For a Cu-2.7% Co alloy the volume fraction of precipitates is approximately 3%, but the signal strength is suppressed approximately 30%. Hummel⁹¹

has investigated a binary two phase system, silver-aluminum, and found that in the two phase field that there was a non-linear optical response to the relative amounts of each phase. Perhaps this type of behavior is seen in the copper-cobalt system as well.

Another possibility is that the precipitates might be influencing a much larger volume than is equal to the volume fraction because they exert strain in the lattice. As long as the precipitates remained coherent, the strain exerted by them would extend into an appreciable volume of the alloy. This strain would have the effect of changing the lattice parameter of the alloy which, in turn, would influence the optical properties. This could account for the large suppression of the signal strength that was observed in the optical properties of the aged alloys.

Finally, the behavior of the feature in the differential reflectograms labelled "c" in Figure 4-8 was examined to determine whether or not the precipitates influenced the optical properties of the alloys. This feature of the differential reflectograms is seen to be formed in the shape of a "well". It is believed to be the result of electronic transitions from cobalt d-bands to the Fermi energy and thus might provide a measure of the amount of cobalt in an alloy. Analysis of the data from the compositional modulation experiments revealed that the depth of this "well" was dependent on the difference in cobalt concentration between two

alloys. Attempts were made to quantify this relationship, but none proved successful. Qualitatively, however, this observation should be noted.

In Figure 4-22 are seen two differential reflectograms. The lower spectrum is a compositional modulation spectrum in which one alloy is Cu-2.7% Co and the other is Cu-1.0% Co. Both alloys were solution heat treated. The upper spectrum is taken from the aging experiments in which both alloys are Cu-2.7% Co, of which one has been solution heat treated and the other has been solution heat treated and fully aged. As has been noted, a fully aged alloy has a matrix solute concentration of 0.4% Co. It is apparent in Figure 4-22 that the depth of the "well" at approximately 3.2 eV is much more shallow in the spectrum from the aging experiments than in the spectrum from the compositional modulation experiments. Qualitatively, this would indicate only a small difference in cobalt content between the aged alloy and the alloy against which it is being compared, perhaps on the order of a few tenths of a percent. Because the difference in solid solution cobalt concentration is known to be 2.3% Co (2.7% Co - 0.4% Co -- the equilibrium solute concentration), it is possible to conclude that the signal contributing to this "well" comes not only from the solute in solid solution, but also from the cobalt in the precipitates. Although this conclusion is somewhat speculative, taken in context with the rest of the data it seems

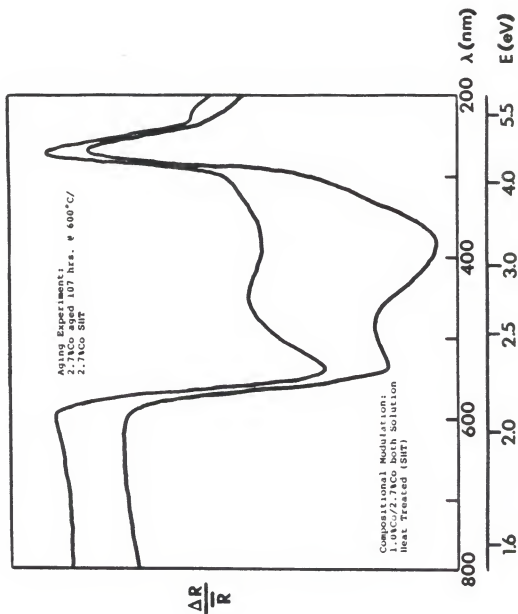


Figure 4-22. Comparison of Spectra from Aging Experiments (Top) and Compositional Modulation Experiments (Bottom).

reasonable. This observation of a shallow "well" was consistent in all of the reflectograms in the aging experiments.

There are several experiments which can be performed to determine more precisely the manner in which the precipitates influence the optical signal in the aged alloys. If the precipitates are exerting strain on the lattice thereby altering the electronic structure of the alloys, it would be valuable to age the alloys for very long times producing a very coarse precipitate structure in which the effects of strain would be minimized. Any changes in the differential reflectometric spectra could be ascribed to a decrease in strain due to coarsening. It must be noted, however, that the microhardness measurements have revealed that the aged alloys are well past peak hardness after being aged for 590 hours at 600°C. No changes in the spectra have been observed past 26 hours of aging, as softening occurred. This may indicate that lattice strain is not a "first order" phenomenon, but spectra taken after very long aging times would still be useful in this regard.

A second experiment would be necessary to determine whether or not the optical signal from the precipitates is independent of the optical signal of the matrix. As was discussed above, the suppression of the signal strength is not in direct relation to the volume fraction of precipitates. It has been noted that a 3% volume fraction of precipitates suppresses the signal strength approximately 30%. If the optical signal of the precipitates were independent of that

of the matrix, one would expect that the magnitude of the suppression would be the same as the volume fraction of precipitates, in this case 3%. It is suggested that the reflectivity of the precipitates -- Co-10% Cu -- be obtained and add an appropriate percentage of this reflectivity to the reflectivity of a solution heat treated Cu-0.4% Co alloy (the equilibrium solute concentration of the alloys). This would provide a situation in which the two reflectivities were completely independent. It would then be possible to determine quantitatively if this reflectivity differed from the reflectivity of an alloy in which the precipitates are actually embedded in the lattice on an aged alloy. This type of analysis would provide a method for determining the precise interaction between the optical properties of the precipitates and the matrix.

Lastly, experiments could be performed which explore the two phase field in the copper-cobalt system. These experiments would be similar in scope to the types of experiments Hummel⁹¹ performed on the silver-aluminum system. They could be designed to explore the optical properties of alloys which contain different amounts of the second phase. With this as the independent variable, the optical properties of the second phase and its interaction with the primary phase might be revealed more precisely.

In conclusion, the validity of the calibration curve obtained from the optical measurements of the aged alloys has been analyzed. It has been reasoned that the aging heat

treatments given to these alloys at 600°C brought the system to a fully aged condition and that the equilibrium solute concentration of 0.4% cobalt was achieved. This permitted analysis of the data on the basis that the difference in solid solution cobalt concentration was known and the points on the lower calibration curve in Figure 4-21 to be accurately placed. It has also been concluded that the suppression of the signal strength at 2.2 eV obtained from optical measurements on aged alloys is caused by the influence of the precipitates on the optical properties of these alloys. The suppression of this signal strength may be due to strain or an interaction of the electronic properties of the precipitates and the matrix. Experiments have been proposed which might reveal the precise influence of the precipitates on the optical properties of these alloys. This additional sensitivity of the differential reflectometer to reveal a difference in microstructural state has not been shown until this study.

4.4 The Kinetics of the Precipitation Reaction

There is disagreement in the literature concerning the time dependency of the precipitation reaction in the copper-cobalt system. There are reports of those researchers 29-31, 33,34,44 who claim that the precipitation reaction occurs so rapidly that it can not be observed as having any time dependency and that all changes in mechanical properties

take place by coarsening of the precipitate structure. Reports^{16,28,38,43,47} also exist that are based on a time dependent rate of growth which follows a time independent nucleation event (site saturation). In one case, both types of behavior have been observed for the precipitation reaction.³⁷ In this investigation, the average solute concentration of the matrix was seen to change with aging time. Because coarsening would involve no change in the solute concentration of the matrix, the results of this investigation indicate a growth process for the precipitation reaction. It remains that the data obtained by these optical measurements yield consistent results when analyzed by a standard model for the precipitates.

In this section, the kinetic data, which were obtained by taking optical measurements of the aged copper-cobalt alloys, will be evaluated quantitatively.

One method employed to follow the transformation kinetics of a solid state reaction is the application of the Avrami equation:

$$X = 1 - \exp(-t/\tau)^n. \quad (5)$$

In this equation, X is the volume fraction transformed; t is the aging time; τ is a time constant, and n is a constant which depends on the shape of the precipitate and other particulars of the reaction. Generally, the volume fraction transformed, X , is obtained and $\log(\ln(1 - X)^{-1})$ is plotted versus $\log t$. This yields a straight line which has a slope

of n . From this determination of a value for the constant, n , the shape of the precipitate can be obtained. Servi and Turnbull³⁸ used this method when studying precipitation in dilute copper-cobalt alloys by means of electrical resistivity measurements. The value of n determined by these researchers varied from 1 to 2 depending on the aging temperature. For diffusion controlled growth, the growth radius depends on $t^{1/2}$. On this basis (an average of 1.5 for n), Servi and Turnbull concluded that the shape of the precipitate was spherical.

It is then necessary to extract information from the differential reflectograms which will relate the measured quantity, the signal strength, to the volume fraction transformed. It has been seen that the signal strength, Σ , at the 2.2 eV minimum is dependent on two factors. One is the difference in matrix solid solution composition between an aged and an unaged sample; the other is the effect of the precipitates. These two effects will now be discussed separately.

As the difference in matrix solid solution composition increases, so does the strength of the optical signal, Σ . On the basis of the difference in composition alone, it can be seen in Figure 4-12 that

$$\Sigma_{\text{comp}}^{\text{meas}} = k\Delta C \quad (6)$$

where Σ is the measured signal strength due to composition effects; ΔC is the difference in matrix composition between

the two samples; and k is equal to the slope of the line.

In the case of one sample having been aged and the other sample having been solution heat treated, it is apparent that

$$\Delta C = C^{\circ} - \bar{C}(t) \quad (7)$$

where C° is the matrix composition for the solution heat treated sample, and $\bar{C}(t)$ is the average matrix composition of the sample after being aged for time, t . Also, using the extremes of the line,

$$k = \frac{\Sigma_{\text{comp}}^{\text{max}}}{C^{\circ} - C^{\alpha}} \quad (8)$$

where $\Sigma_{\text{comp}}^{\text{max}}$ is equal to the maximum signal strength measured, which occurs when $\Delta C = C^{\circ} - C^{\alpha}$, where C^{α} is equal to the maximum solid solubility for cobalt in copper at a particular aging temperature.

Substituting the expression for ΔC and k into Equation 5 yields

$$\Sigma_{\text{comp}}^{\text{meas}} = \Sigma_{\text{comp}}^{\text{max}} \left\{ \frac{C^{\circ} - C(t)}{C^{\circ} - C^{\alpha}} \right\}. \quad (9)$$

Further,

$$\begin{aligned} \frac{\Sigma_{\text{comp}}^{\text{meas}}}{\Sigma_{\text{comp}}^{\text{max}}} &= \frac{C^{\circ} - \bar{C}(t)}{C^{\circ} - C^{\alpha}} \\ &= 1 - \frac{\bar{C}(t) - C^{\alpha}}{C^{\circ} - C^{\alpha}} \end{aligned} \quad (10)$$

The right side of the equation is equal to X , the volume fraction transformed. Therefore, for composition effects

only the volume fraction transformed can be obtained as the ratio of the measured signal strength to the maximum signal strength:

$$X = \frac{\Sigma_{\text{comp}}^{\text{meas}}}{\Sigma_{\text{comp}}^{\text{max}}}. \quad (11)$$

It has been seen, however, that the signal strength is diminished by the presence of precipitates. Furthermore, it has been demonstrated that the greater the amount of precipitates present, the greater is the suppression of the signal strength. If this suppression of the signal strength is proportional to the volume fraction, then

$$\Sigma^{\text{meas}} = X \Sigma_{\text{comp}}^{\text{max}} - X \Sigma_{\text{precip}}^{\text{max}} \quad (12)$$

where Σ^{meas} is the measured value of the signal strength, and $\Sigma_{\text{precip}}^{\text{max}}$ is the maximum amount of suppression, which is caused by a sample that is fully aged. It can be concluded, therefore, that the volume fraction transformed can be obtained by the following equation:

$$X = \frac{\Sigma^{\text{meas}}}{\Sigma_{\text{comp}}^{\text{max}} - \Sigma_{\text{precip}}^{\text{max}}}. \quad (13)$$

The data from the optical measurements of the aged copper-cobalt alloys were treated in this way in order to determine the constant, n , in the Avrami equation. The results of these calculations can be seen in Table 4-2, which lists n for various compositions and aging temperatures. As can be seen all values for n fall in a narrow range of

Table 4-2. Functional Dependency, n , of the Exponent
in the Avrami Equation

<u>Composition</u>	<u>Temperature</u>	<u>n</u>
2.7% Co	600°C	.91
2.7% Co	500°C	.84
2.0% Co	600°C	.87
2.0% Co	500°C	.84
1.0% Co	600°C	.89
1.0% Co	500°C	.85

slightly less than one. A value of $n = 1$ can be interpreted, in the case of site saturation, diffusion controlled growth, as the growth of precipitates in the shape of platelets.

The result that the precipitates grow in the shape of platelets contradicts a general result of other studies of this system. That is, most researchers have reported that the precipitates in this system grow as spheres.

There are two possibilities that may explain this discrepancy. Firstly, the method by which the alloys in this work were handled might have produced platelets. It must be recalled that the ingots were rolled by approximately 75% after they were made. After this step, they were recrystallized. It is possible that some texture remained as a result of the rolling step. This could have had the effect of producing preferred planes on which the precipitates nucleated to form platelets. Performing TEM on sections of the alloys would determine the shape of the precipitates.

Secondly, although the model used to interpret these results produced a consistent value of n , the model is based on the assumption that the lower calibration curve in Figure 4-21 is correct in that the suppression of the signal strength is linearly dependent on the fraction transformed. Because the effect of the precipitates on the optical signal is not precisely known at this time, it is possible that the interaction of the optical signal between the precipitates and the matrix is more complicated than this simple relationship.

The experiments outlined in the previous section should facilitate a more precise interpretation of this relationship.

Finally, the kinetics of the reaction for this work were compared with data analyzed from other research efforts.^{37, 38,89} In Figure 4-23, the fraction transformed is plotted as a function of time for alloys of varying cobalt content aged at 600°C. When compared with themselves, the data from this work show a slight increase in the fraction transformed as the cobalt concentration increases. This is explainable by the larger driving force for precipitation that exists the farther an alloy concentration is from equilibrium. When compared with the other data obtained for this system, it can be seen that the kinetics of the reaction in this work are slightly slower than the rates reported by Witt and Gerold³⁷ for Cu-1.4% Co and Gerold⁹², but overall the values fit into a middle range of all the values reported.

4.5 Comparison of Microhardness and Optical Results

In this section, a comparison of the results of the microhardness and the differential reflectometer measurements will be presented. The data from these two techniques provide overlapping and straightforward evidence of the method by which the precipitation reaction in the Cu-Co system proceeds. For the reason that the discussion of this

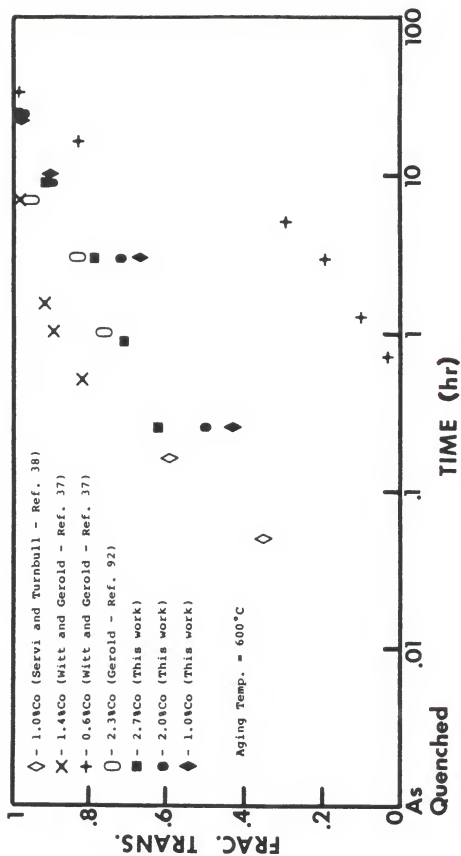


Figure 4-23. Fraction Transformed vs Time at 600°C.

data can be extended to the other two alloy compositions that were investigated in this work, Cu-2.7% Co will be examined in detail.

In Figures 4-24 to 4-26, microhardness data and optical data are shown as a function of aging time, for the three aging temperatures -- 600°C, 500°C, and 400°C -- respectively. In Figure 4-24 a characteristic hardness curve is seen. The immediate sharp rise in the microhardness of the alloy aged at 600°C is accompanied by a large increase in the signal strength in differential reflectivity. This signal strength has been determined to be caused by a depletion of solute from the matrix in the alloy. Further aging leads to more depletion of the alloy matrix as evidenced by the growing signal strength of the optical measurements. A continued increase in hardness corresponds to this depletion. The optical signal strength ceases its growth after approximately 25 hours of aging, signalling an end to the precipitation reaction. Although the hardness of the alloy continues to rise for a time as the solute depletion occurs, the peak hardness of the alloy is achieved before the reaction is complete, as determined optically. This peak is expected and occurs after approximately nine hours of aging.

Figure 2-2 shows that there are four factors which contribute to the decrease of hardness prior to "complete" solute depletion: recrystallization, depletion of the solid solution, coalescence or coarsening of the precipitate structure, and loss of particle coherency. For the dilute Cu-Co

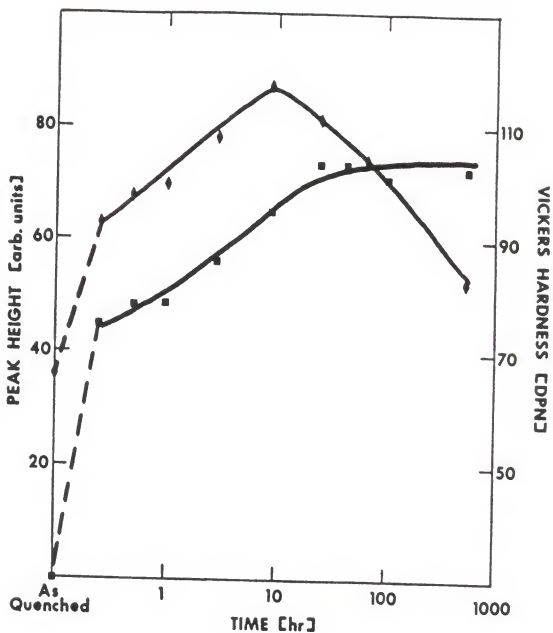


Figure 4-24. Peak Height and Hardness vs Time for Cu-2.7% Co Aged at 600°C.

alloys used in this work, recrystallization at 600°C occurs very rapidly and would not contribute to the hardness curve in a time dependent manner. Although there is some solid solution hardening (see Figure 4-1), its contribution to the hardness is small and therefore the depletion of solute from the matrix would not cause a great loss of hardness. Because the precipitation reaction is not completed (precipitates are still being added to the system) before the alloy begins to lose hardness, it is unlikely that the particle spacing is becoming larger. Therefore, the loss of hardness must correspond to the loss of coherency of the precipitates with the matrix.

One point of contrast between the findings of this work and that of several other reports in the literature is the time necessary for the precipitation reaction to be complete. Although there is agreement between the data of this work and data in the literature concerning the time to achieve a maximum in mechanical properties (see Table 2-1), there are a number of studies in the literature that state that at 600°C the precipitation reaction is complete within fifteen minutes of aging. Therefore, increases in the mechanical properties of Cu-Co after this time must be accomplished by the growth of precipitates by coarsening.

However, all of the data presented in the literature is by no means consistent. There are other reports which support a more gradual depletion of solute from the matrix. Tauzenberger and Gerold⁴⁸ show both types of precipitation

rates at 600°C, depending on the amount of cobalt in copper. The findings of this work can only be interpreted that for aging at 600°C, the precipitation reaction takes between 15-25 hours to complete.

In Figure 4-25 the comparative data of microhardness and optical measurements for Cu-2.7% Co aged at 500°C are presented. It can be seen that the more moderate rate of depletion of solute is accompanied by a more moderate increase in microhardness. It is also evident that neither has the microhardness reached a peak nor has the depletion of matrix solute been completed even after 100 hours of aging. Because the diffusion rate is much slower at 500°C, these data conform well to precipitation theory. In addition, they are self-consistent.

In Figure 4-26, data are presented for Cu-2.7% Co aged at 400°C. At this temperature, the diffusion rate is so low that there is only a slight depletion of solute. The microhardness data confirm this by exhibiting a minute increase.

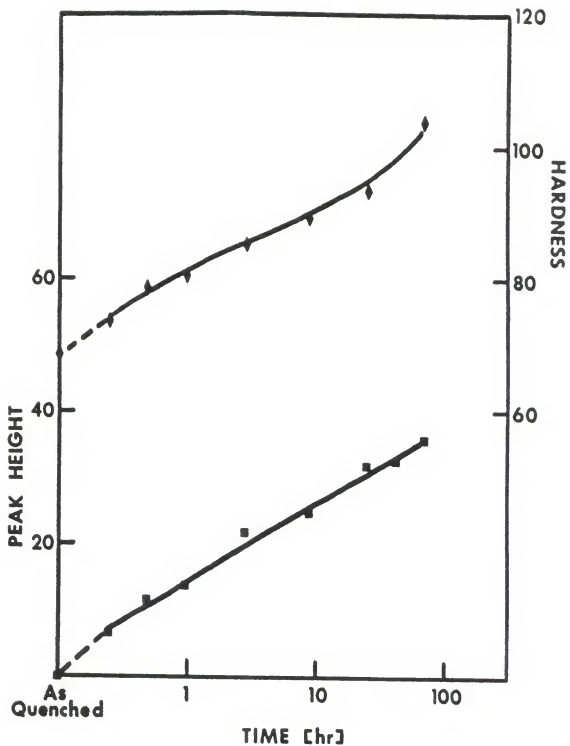


Figure 4-25. Peak Height and Hardness vs Time for Cu-2.7% Co Aged at 500°C.

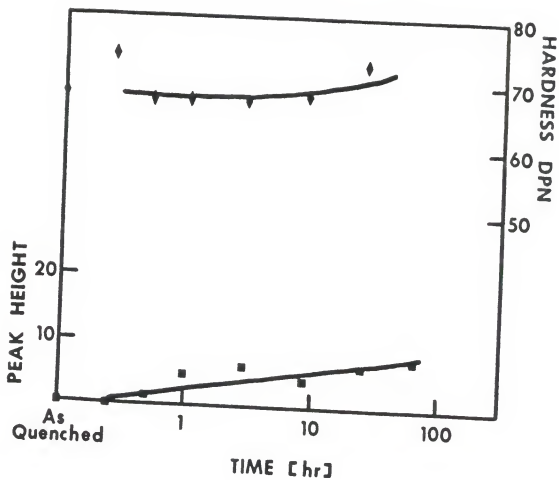


Figure 4-26. Peak Height and Hardness vs Time for Cu-2.7% Co Aged at 400°C.

CHAPTER 5

SUMMARY

In this work, differential reflectometry has been used to investigate the effect of cobalt additions on the electronic band structure of copper and to determine the kinetics of the precipitation of the cobalt-rich phase from dilute copper-cobalt solid solutions. The latter research is the first instance that differential reflectometry has been used to identify the kinetics of a phase transformation.

It has been demonstrated that additions of up to 2.7% cobalt in copper do not change the energy of the copper threshold transition. Investigations of other copper electronic transitions also revealed no solute dependence, except for the peak revealing electronic transitions from the lower d-bands of copper to the Fermi energy, which showed a very slight increase in energy with increased cobalt content. This behavior replicates that observed by other researchers, who studied the effects of nickel additions on the band structure of copper. This common pattern of optical property behavior for the class of copper-transition metal alloys can be accounted for by the phenomenon of virtual-bound states for both cobalt and nickel. For this first time, optical measurements have been used to demonstrate this shared behavior.

Differential reflectometry has clearly revealed that as the difference in solute content between two samples is increased the signal strength of the differential reflectograms is increased. The signal strength of the copper threshold transition, seen as a minimum at 2.2 eV in the differential reflectograms of dilute copper-cobalt alloys, was chosen as the basis for measuring the magnitude of the signal strength. A straightforward linear dependence of the magnitude of the signal strength on the difference in solid solution solute content was found. Quantitatively, the change in the magnitude of the signal strength is $3\%/\Delta\%C$.

Differential reflectometry has also been used to closely monitor the depletion of solute from the matrix during a precipitation reaction. Such a study offers additional information about the electronic structure of alloys, since not only do the compositions of the samples differ -- as in the above-mentioned comparison of solid solution alloys -- but so do the physical states of the alloying constituents. The magnitude of the signal strength of the 2.2 eV minimum has been demonstrated to be a measure of the progress of the precipitation of a cobalt-rich second phase in these dilute copper-cobalt alloys. While observing the precipitation reaction for three different temperatures (600°C, 500°C, and 400°C) and for three different cobalt concentrations (Cu-2.7% Co, Cu-2.0% Co, and Cu-1.0% Co), it has been determined that the higher the aging temperature the faster the reaction occurs. At 600°C, the reaction is complete

between 15-25 hours of aging for all solute concentrations. This finding is consistent with microhardness measurements performed on precipitation hardened alloys. It has further been determined, by the monotonic depletion of solute from the matrix as aging continued, that the hardening observed in these alloys takes place due to growth of the precipitate, as opposed to coarsening of the precipitate structure.

Because the cobalt-rich precipitate in this system has no strong electronic transitions in the spectral range of the differential reflectometer, the precipitates were found not to produce any new feature on the differential reflectograms by which their growth could be followed. However, it has been determined that the magnitude of the signal strength was suppressed as a result of the influence of the precipitates on the optical signal.

To conclude, this work has contributed in the following ways to the understanding of metals:

- 1) This work has verified the common behavior in the electronic structure of copper-cobalt and copper-nickel alloys.
- 2) This work has provided a method by which optical and mechanical properties can be coupled to reveal the nature of a precipitation reaction.
- 3) This work has provided a demonstration that differential reflectivity is sensitive not only to differences in composition, but also to the physical state of the material under investigation.

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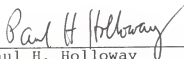
The author is a member of The American Physical Society, The American Vacuum Society, and The American Association of Physics Teachers.

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